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(57) Abstract

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OXIDATION PROCESS IN THE PRESENCE OF CARBON DIOXIDE

The present invention relates to an oxidation process and in particular to a process for the oxidation of unsaturated hydrocarbons in the presence of catalyst under heterogeneous conditions.

It is well known that the epoxidation of unsaturated hydrocarbons e.g. olefinic compounds, with various oxidants such as hydrogen peroxide may be effectively catalyzed by certain synthetic zeolites containing metal atoms such as titanium atoms (see, for example, U.S. Pat. No. 4,833,260).

Various process modifications have been proposed to improve the conversion and selectivity of these oxidation reactions. U.S. Pat. No. 4,824,976 proposes that the non-selective ring-opening reactions which take place when epoxidation is performed in a protic medium such as water or alcohol may be suppressed by treating the catalyst prior to the reaction or during the reaction with a suitable acid neutralising agent. The neutralising agent is said to neutralise acid groups on the catalyst surface which tend to promote by-product formation

U.S. Pat. No. 5,675,026 proposes the addition of neutral- or acid-reactive salts to the catalyst before or during the reaction to improve catalyst activity. U.S. Pat. No. 4,483,996 discloses a process for the conversion of olefins to olefin oxides and ketones. The process utilises a thallous catalyst, with molecular oxygen as oxidant in an aqueous carbon dioxide solvent. U.S. Pat. No. 5,591,875 proposes an epoxidation process which

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utilises a chelating agent to reduce the catalysts tendency to non-selectively decompose the hydrogen peroxide oxidant used. EP 0 385 631 A1 describes an oxidation process for the conversion of olefins to glycols utilising oxygen and carbon dioxide as reactants under supercritical conditions. A heterogeneous copper containing catalyst is proposed. U.S. Pat. No. 5,646,314 proposes performing the oxidation reaction in the presence of nonbasic salts in order to improve selectivity.

Furthermore it has long been recognised that metal containing zeolite catalysts rapidly become deactivated in use. There have been a number of methods developed to counter this deactivation and/or to regenerate the catalyst after use. U.S. Pat. No. 5, 741, 749 proposes a the regeneration of a titanium containing molecular sieve oxidation catalyst by treatment with a gas stream comprising specific amounts of molecular oxygen. WO 98/18555 proposes the regeneration of a titanium silicalite catalyst with a liquid solution of an oxidising agent. WO 98/ 18556 proposes the regeneration of a titanium silicalite catalyst under a specific gas flow

There are a number of problems with the processes of the prior art. Conversions and selectivities for the various reactions are in general still low or require additional process modifications which incur additional costs. Frequently the catalyst systems utilised require special treatments and/or frequent regeneration in order to maintain catalyst activity.

It has been surprisingly found that the conversion and selectivity of oxidation processes, in particular the

conversion of unsaturated hydrocarbons, especially olefins, to oxidation products especially oxirane compounds, are significantly improved by utilising a specific group of catalysts in the presence of carbon dioxide. It has also been surprisingly found that the heterogeneous catalysts of the present process maintain their activity for significantly longer periods of time and through many recycles through the process. This improved activity with respect to the catalyst means that costly and laborious pre-treatments and/or regenerations of the catalyst are either not required or are required at less frequent intervals in the process of the present invention compared to prior art processes.

Accordingly the present invention provides a process for the conversion of one or more unsaturated hydrocarbons to one or more oxidation products which process comprises reacting one or more unsaturated hydrocarbons in a reaction mixture under oxidation conditions in the presence of an oxidant, heterogeneous catalyst and a solvent characterised in that the catalyst comprises a Group IVB, VB or VIB metal and that carbon dioxide is present in the reaction mixture.

In a preferred embodiment, the present invention pertains to an epoxidation process wherein a titanium containing catalyst is utilised in the presence of hydrogen peroxide as oxidant and the carbon dioxide is present in the reaction mixture under supercritical conditions.

Suitable oxidants for the process of the present invention may be hydrogen peroxide or hydroperoxides. Examples of hydroperoxides include tert-butyl hydroperoxide (TBHP) and ethyl benzene hydroperoxide

(EBHP). The preferred oxidant for the process of the present invention is hydrogen peroxide (H_2O_2). Hydrogen peroxide (H_2O_2) utilised as the oxidant in the present invention may be obtained from any suitable source, including, for example, from autoxidation of secondary alcohols using air or other source of molecular oxygen. Suitable secondary alcohols include both aliphatic alcohols such as isopropanol and cyclohexanol as well as aromatic alcohols such as alpha methyl benzyl alcohol and anthrahydroquinones (including alkyl-substituted anthrahydroquinones). The crude reaction product thereby generated may be either used directly in the epoxidation process of this invention or, if so desired, purified, fractionated, concentrated, ion exchanged, or otherwise processed prior to such use. For example, the ketone generated as an autoxidation co-product may be separated, in whole or in part, from the hydrogen peroxide by distillation (where the ketone is relatively volatile) or by extraction with water (where the ketone is substantially immiscible with or insoluble in water). The hydrogen peroxide may alternatively be generated in situ by, for example, combining oxygen, secondary alcohol, olefin, and catalyst within a reaction zone under conditions effective to accomplish simultaneous secondary alcohol autoxidation and olefin epoxidation. Generally speaking, it will be desirable to employ initial hydrogen peroxide concentrations of from about 1 to 20 weight per cent in the liquid phase within the reaction zone.

The unsaturated hydrocarbon is preferably an organic compound having from two to thirty carbon atoms and at least one ethylenically unsaturated functional group (i.e. a carbon-carbon double bond) and may be a cyclic, branched or straight chain aliphatic olefin. More than

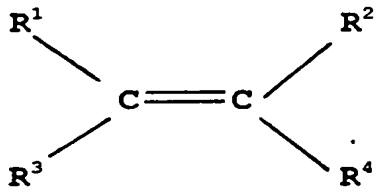
one carbon-carbon double bond may be present in the olefin, dienes, trienes, and other polyunsaturated substrates thus may be used.

Exemplary olefins suitable for use in the process of this invention include ethylene, propylene, the butenes, butadiene, the pentenes, isoprene, hexenes, heptenes, octenes, diisobutylene, nonenes, the trimers and tetramers of propylene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclooctadiene, dicyclopentadiene, methylenecyclopropane, methylenecyclopentane, methylenecyclohexane, vinylcyclohexane, and vinyl cyclohexene. Preferred olefins are 1-octene, propylene and cyclopentene.

Mixtures of olefins may be epoxidized and resulting mixture of epoxides either employed in mixed form or separated into the different component epoxides. One example of a preferred olefin mixture is a raffinate mixture which comprises mixed butenes; 1-butene, cis-2-butene, trans-2-butene and iso-butene.

The resulting epoxide or epoxide mixture may be rearranged to the corresponding linear aldehyde or ketone, either in-situ or in a separate step. Subsequent oxidation or hydrogenation of the aldehyde will result in the corresponding linear acid or linear alcohol. Subsequent hydrogenation of the ketone wil result in secondary alcohols.

The process of this invention is especially useful for the epoxidation of C_2-C_{10} olefins having the general structure:



wherein R^1, R^2, R^3, and R^4 are the same or different and are selected from the group consisting of hydrogen and C_1-C_8 alkyl (selected so that the total number of carbons in the olefin does not exceed 30).

The process of this invention is also suitable for use in epoxidizing olefins containing functional groups other than aliphatic hydrocarbyl moieties. For example, the carbon-carbon double bond can be substituted with groups such as $-CO_2H$, $-CO_2R_1$, -CN, or -OR wherein R is an alkyl, cycloalkyl, aryl or aralkyl substituent. The radicals R^1, R^2, R^3, and R^4 in the structural formula shown hereinabove may contain aryl, aralkyl, halo, nitro, sulfonic, cyano, carbonyl, (e.g. ketone, aldehyde,) hydroxyl, carboxyl (e.g ester, acid) or ether groups. Examples of olefins of these types include allyl alcohol, styrene, allyl chloride, allyl methyl ether, allyl phenyl ether, methyl methacrylate, acrylic acid, methyl acrylate, stilbene, and the like.

The amount of hydrogen peroxide relative to the

amount of olefin is not critical, but most suitably the molar ratio of olefin: hydrogen peroxide is from about 100:1 to 1:10 when the olefin contains one ethylenically unsaturated group. The molar ratio of ethylenically unsaturated groups in the olefin to hydrogen peroxide is more preferably in the range of from 1:2 to 10:1.

The heterogeneous catalysts contain a Group IVB (e.g. Ti, Zr or Hf), VB (e.g. V, Nb or Ta) or VIB (e.g. Cr, Mo or W) metal and may be crystalline and/or amorphous. The most preferred catalysts contain a Group IVB metal. Particularly preferred catalysts are crystalline molecular sieves especially zeolites which contain titanium.

The titanium silicalites useful as catalysts in the epoxidation step of the process comprise the class of zeolite substances wherein titanium is substituted for a portion of the silicon atoms in the lattice framework of a molecular sieve. Such substances are well-known in the art.

Particularly preferred titanium silicalites include the classes of molecular sieves commonly referred to as "TS-1" (having an MFI topology analogous to that of the ZSM-5 aluminosilicate zeolites), "TS-2" (having an MEL topology analogous to that of the ZSM-11 aluminosilicate zeolites), and "TS-3" (as described in Belgian Pat. No. 1,001,038). Also suitable are the titanium-containing molecular sieves having framework structures isomorphous to zeolite beta. Also suitable is TS-48 with the structure of zeolite ZSM-48 as well as titanium mordenite with the MOR structure. The titanium silicalite preferably contains no non-oxygen elements other than titanium and silica in the lattice framework, although

minor amounts of boron, iron, aluminum, and the like may be present.

Titanium silicalite catalysts suitable for use in the process of this invention will generally have a composition corresponding to the following empirical formula $xTiO_2:(1-x)SiO_2$, where x is between 0.0001 and 0.500. More preferably, the value of x is from 0.01 to 0.125. The molar ratio of Si:Ti in the lattice framework of the titanium silicalite is advantageously from 9.5:1 to 99:1 (most preferably, from 9.5:1 to 60:1). The use of relatively titanium-rich silicalites may also be desirable. The preferred catalyst is titanium silicalite-1. One form of catalyst suitable for use in the process of the present invention is a "cherry type" catalyst which consists of a core of material e.g. silica/alumina and a shell of different material e.g. silica/titania as described for example in EP 634 212. The titanium silicalite catalyst may be incorporated in or in the form of a membrane; for example TS-1 or Ti-MCM-41 may be occluded in polydimethylsiloxane (PDMS) membranes, as described in Chemical Communications (1997) pages 137 to 138.

The amount of catalyst employed is not critical, but should be sufficient so as to substantially accomplish the desired epoxidation reaction in a particularly short period of time. The optimum quantity of catalyst will depend upon a number of factors including reaction temperature, olefin reactivity and concentration, hydrogen peroxide concentration, type and concentration of organic solvent as well as catalyst activity and the type of reactor or reaction system (i.e. batch vs continuous) employed. In a batch-type or slurry reaction, for example, the amount of catalyst will

typically be from 0.001 to 10 grams per mole of olefin. In a fixed or packed bed system, the optimum quantity of catalyst will be influenced by the flow rate of reactants through the fixed bed; typically, from about 0.05 to 2.0 kilograms hydrogen peroxide per kilogram catalyst per hour will be utilised. The concentration of titanium in the liquid phase reaction mixture will generally be from about 10 to 10,000 ppm.

The catalyst may be utilised in powder, pellet, microspheric, extruded, monolithic or any other suitable physical form. The use of a binder (co-gel) or support in combination with the titanium silicalite may be advantageous. Supported or bound catalysts may be prepared by the methods known in the art to be effective for zeolite catalysts in general. Preferably, the binder or support is essentially non-acidic and does not catalyze the non-selective decomposition of hydrogen peroxide or ring-opening of the epoxide. Two or more heterogeneous catalysts may be used if desired.

Illustrative binders and supports include titania, silica, alumina, silica-alumina, silica-titania, silica-thoria, silica-magnesia, silica-zirconia, silica-beryllia, and ternary compositions of silica with other refractory oxides. Also useful are clays such as montmorillonites, koalins, bentonites, halloysites, dickites, nacrites, and ananxites. The proportion of titanium silicalite binder or support may range from 99:1 to 1:99, but preferably is from 5:95 to 80:20.

The epoxidation reaction temperature is preferably from 0°C to 100°C (more preferably from 40°C to 80°C), which has been found to be sufficient to accomplish selective conversion of the olefin to epoxide within a

reasonably short period of time with minimal non-selective decomposition of the hydrogen peroxide. It is generally advantageous to carry out the reaction to achieve as high a hydrogen peroxide conversion as possible, preferably at least 50%, more preferably at least 90%, most preferably at least 99%, consistent with high selectivities. The optimum reaction temperature will be influenced by catalyst concentration and activity, substrate reactivity, reactant concentrations and type of solvent employed, amongst other factors.

Reaction or residence times of from about 10 minutes to 48 hours will typically be appropriate, depending upon the above-identified variables. One advantage of the present invention however is that the reaction time required to achieve near quantitative conversion of the oxidant may be considerably shorter compared with those reactions undertaken in the absence of CO_2. This reduction in reaction time may be as much as 20% or even 50% or more. Thus the reaction residence time is at least 20% less and more preferably at least 50% less, than that required for 50%, more preferably 90% and most preferably 99% conversion of the oxidant, in a reaction without the presence of carbon dioxide.

The reaction is performed at elevated pressure (typically, between 1 and 700 atmospheres). Generally, it will be desirable to maintain the reaction components as a liquid mixture. For example, when an olefin such as propylene is used having a boiling point at atmospheric pressure which is less than the epoxidation temperature, a superatmospheric pressure sufficient to maintain the desired concentration of propylene in the liquid phase is preferably utilised.

The epoxidation process of this invention may be

carried out in a batch, continuous, or semi-continuous manner using any appropriate type of reaction vessel or apparatus such as a fixed bed, transport bed, stirred slurry, or CSTR reactor. Known methods of conducting metal-catalysed epoxidations using hydrogen peroxide will generally also be suitable for use. Thus, the reactants may be combined all at once or sequentially. For example, the hydrogen peroxide and/or the olefin may be added incrementally to the reaction zone.

The oxidation must be carried out in the presence of carbon dioxide in the gaseous, liquid or supercritical state. It is most preferred that the carbon dioxide is present in the supercritical state which is where it exists as a one phase fluid occurring above both a critical temperature and pressure Tc and Pc, which is 31°C and 73.8 kg/cm^2. The reaction mixture including catalyst comprises at least 1% by weight of carbon dioxide, preferably at least 10% by weight and more preferably at least 25% by weight of the reaction mixture including catalyst. In a most preferred embodiment the carbon dioxide constitutes more than 50% by weight of the solvent used in the reaction mixture.

Any solvent or combination of solvents which are compatible with carbon dioxide may be used. The preferred solvent has methanol as its main constituent in combination with carbon dioxide. Other suitable solvents include, but are not limited to water alcohols (especially C_1-C_{10} aliphatic alcohols such as isopropanol), ketones (especially C_3-C_{10} ketones such as acetone), and mixtures of such solvents. It is preferred that supercritical carbon dioxide is present as the solvent or in admixture with other solvents. Accordingly carbon dioxide when present as a solvent should be at

least 1% by weight of the solvent mixture and preferably at least 5 to 100%, most preferably 25 to 100% by weight of the solvent. In a most preferred embodiment the carbon dioxide comprises at least 50% by weight of the solvent. The total amount of solvent in the reaction mixture will depend on a number of factors including the nature of the substrate being oxidised, the form and nature of introduction of the oxidant and the amount of CO_2 present. It has surprisingly been found that in the process of the present invention the ratio of solvent to substrate (unsaturated hydrocarbon or hydrocarbons being oxidised) may be significantly less than that required using the typical reaction conditions described in the art. This has the benefit of either enabling the reactor capacity to be better utilised or to enable the economic use of smaller reactors. In addition the requirement for less solvent results in less solvent recycle and a more energy efficient process. Typically reaction conditions in the art require solvent to substrate ratios of 8:1 or more. In the process of the present invention it is possible to use solvent to substrate ratios of less than 8:1 preferably 7:1 or less and most preferably 4:1 or less or 2:1 or less. Solvent to substrate ratios as low as 1:1 may be used; accordingly it is preferred that the ratio is within the range of 8:1 to 1:1 and most preferably 7:1 to 1:1 or narrower ranges based on the upper limits identified. Reduction of the ratio, when using the typical reaction conditions in the art, results in inefficient utilisation of the oxidant due to unwanted side reactions. In the process of the present invention the reduction in the ratio does not have a marked detrimental effect on oxidant efficiency which is significantly maintained at even the lowest ratios.

Once the epoxidation has been carried out to the

desired degree of conversion, the epoxide product may be separated and recovered from the reaction mixture using any appropriate technique such as fractional distillation, extractive distillation, liquid-liquid extraction, crystallisation, or the like. After separating from the epoxidation reaction mixture by any suitable method such as filtration (as when a slurry reactor is utilised, for example), the recovered titanium silicalite catalyst may be economically re-used in subsequent epoxidations. Where the catalyst is deployed in the form of a fixed bed, the epoxidation product withdrawn as a stream from the epoxidation zone will be essentially catalyst free with the catalyst being retained within the epoxidation zone. Similarly, any unreacted olefin or hydrogen peroxide may be separated and recycled or otherwise disposed of. In certain embodiments of the instant process where the epoxide is produced on a continuous basis, it may be desirable to periodically or constantly regenerate all or a portion of the used catalyst in order to maintain optimum activity and selectivity. Suitable regeneration techniques are well-known and include, for example, calcination and solvent treatment. Such regeneration and/or treatment may not be necessary until a significant number of recycles have occurred through the process of the present invention. Typical examples of suitable regeneration methods are provided in WO99/01445, WO98/18556, WO98/28072 and Journal of Molecular Catalysis A:Chemical 117 (1997) 351-356. The disclosures of each of these references are incorporated by reference.

From the foregoing description, one skilled in the art can readily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof can make various changes and

modifications of the invention to adapt it to various usages, conditions, and embodiments.

The present invention is further illustrated by means of the following examples:

Example 1

A TS-1 catalyst (prepared by the procedure given in Applied Catalysis, 99, (1993), pages 71-84) was utilised in the oxidation of 1-octene to 1,2-epoxyoctane with and without supercritical carbon dioxide as the solvent. A 250 cm^3 batch autoclave equipped with a temperature controller, mechanical stirrer (1000 rpm), reagents feed line, sampling line and vent line was charged in two separate experiments with the following reagents.

Reagents	Experiment 1	Experiment 2
	Weight (g)	Weight (g)
1-octene	14.52	7.26
H_2O_2 (30wt% in H_2O)	0.44*	0.22*
Methanol	112.5	56.25
Carbon Dioxide	0	74.2
TS-1 catalyst	1.0	0.5
Total	128.46	138.43

*= the weight of H_2O_2 does not include the weight of H_2O

For Experiment 1 the reaction was undertaken at 65°C for 60 minutes. For Experiment 2 the reactor was first pressurised with carbon dioxide gas to 48 bar (48 x 10^5 Nm^{-2}), after which 74.2g of liquid carbon dioxide was

added. The reaction was undertaken at 65°C for 60 minutes and at a pressure of 106 bar (106×10^5 Nm^{-2}). The composition of the reaction mixtures was determined using Gas Chromatography and the hydrogen peroxide content was determined using iodometric titration.

The results are provided in Table 1.

Table 1

Experiment	Mole % 1,2-epoxyoctane	Mole % Glycolethers	% Conversion of H_2O_2
1	77.8	22.2	97.9
2	91.1	8.9	98

It can be seen from the above results that for a given conversion the selectivity is greatly enhanced when carbon dioxide is used in the oxidation utilising TS-1 as catalyst.

Example 2

In a further set of experiments the solvent system utilised was methanol or methanol/CO_2 under supercritical conditions.

In a first set of experiments (Experiment 3) the TS-1 catalyst was used in a methanol solvent and recycled without treatment or regeneration. In a second set of experiments (Experiment 4) the TS-1 catalyst was used in a methanol/carbon dioxide solvent system under supercritical conditions with respect to the carbon dioxide again the catalyst was recycled without further treatment or regeneration.

Methanol Solvent - Catalyst Recycle

The following reagents were used:

Reagents	Experiment 3
	Weight (g)
1-octene	7.26
H_2O_2 (30wt% in H_2O)	0.22*
Methanol	56.3
Carbon Dioxide	0
TS-1 catalyst	0.5
Total	64.23

*= the weight of H_2O_2 does not include the weight of H_2O

The reaction was undertaken at 40°C for 60 minutes in a 100 cm^3 glass reactor with magnetic stirrer and chilled water cooler on an electrical heating mantle. On completion the reactor was recharged with reagents and the used catalyst was recycled by filtration and drying in vacuo at room temperature for 10 minutes. The catalyst was recycled four times and the results are provided in Table 2.

Table 2			
Run Number	Mole % 1,2-epoxyoctane	Mole % Glycolethers	%Conversion of H_2O_2
1.Fresh catalyst	89.5	10.5	90.1
2.First recycle	100	0	52.0
3.Second recycle	100	0	28.4
4.Third recycle	100	0	21.1
5.Fourth recycle	100	0	17.1

It can be seen from the results in Table 2 that the conversion of hydrogen peroxide is dramatically reduced on recycling the catalyst.

Methanol Solvent with Carbon Dioxide - Catalyst Recycle

The following reagents were used:

Reagents	Experiment 4
	Weight (g)
1-octene	7.26
H_2O_2 (30wt% in H_2O)	0.22*
Methanol	56.25
Carbon Dioxide	82.8
TS-1 catalyst	0.5
Total	147.03

*= the weight of H_2O_2 does not include the weight of H_2O

A 250 cm^3 batch autoclave equipped with a temperature controller, mechanical stirrer, reagents feed line, sampling line and vent line was filled with all the above reagents except carbon dioxide and 1-octene. Then the reactor was pressurised with carbon dioxide gas to 52 bar (52 x 10^5 Nm^{-2}), after which 82.6g of liquid carbon dioxide was added, then 1-octene was injected and the reaction was undertaken at 40°C for 30 minutes and at a pressure of 74.3 bar (74.3 x 10^5 Nm^{-2}). On completion of the reaction the catalyst was removed by filtration and dried in air before being twice recycled using the same reactor, reagents and conditions. The results are provided in Table 3.

Table 3

Run Number	Mole % 1,2-epoxyoctane	Mole % Glycolether	%Conversion of H2O2
1.Fresh catalyst	100	0	96
2.First recycle	100	0	96
3.Second recycle	100	0	88
4.Third recycle	100	0	36.6
5.Fifth recycle	100	0	37.6

It can be seen from the results in Table 3 that utilising carbon dioxide in the reaction enables the catalyst to be recycled without a dramatic reduction in hydrogen peroxide conversion whilst maintaining a high selectivity towards the desired epoxide. The results are illustrated in Figure 1, which shows the % conversion for each recycle. Figure 2 illustrates the stability of a catalyst

in pellet form, over 10 reaction recycles, under the process conditions of experiment 4 of this example. Between 70 to 80% of the original catalyst weight was recovered at the end of the recycle. Some of the reduced conversion identified in Figures 1 and 2 is not due to catalyst deactivation but is due to catalyst losses from the reactor. Figure 3 illustrates the conversion with and without carbon dioxide using turnover number (TON). Turnover number corrects for the effects of catalyst losses from the reactor between reaction cycles and is a calculated as follows for each reaction period:

TON = mmol of epoxide / mmol of titanium in the catalyst

The results in Figure 3 show that when methanol is used as the solvent there is a dramatic reduction in catalyst effectiveness after four reaction cycles whereas when carbon dioxide is utilised according to the invention there is no significant reduction in catalyst activity after the same number of cycles.

Example 3

Example 1 was repeated with the exception that the reaction time was 30 minutes and the reaction temperature was 40°C. The results are provided in Figure 4; these results illustrate that at short reaction times and low temperature the process of the invention provides improved selectivity and oxidant conversion.

Example 4

The general procedure of example 1 experiment 2 was repeated using a raffinate-2 feedstock in place of the 1-octene. The raffinate-2 feedstock comprised 29.9 wt% of 1-butene, 21.6 wt% of cis-2-butene, 36.8 wt% of trans-2-butene and 1.9 wt% of iso-butene.

In the reaction the following proportions and conditions were used: 3.6 g (58.3 mmol) of butenes; 0.656 g (5.8 mmol) of H_2O_2 (as a 30% solution in H_2O); 0.5 g of TS-1 pellets; 50 g methanol; and a CO_2 pressure of 89 bar for 1 hour at 40°C.

The reaction resulted in 98.2% selectivity for the epoxides compared with a selectivity of 93% without the use of carbon dioxide.

Example 5

The general procedure of example 1 was repeated using a cyclopentene feedstock in place of the 1-octene.

In the reaction the following proportions and conditions were used: 3.93 g (58.3 mmol) of cyclopentene, 0.656 g (5.8 mmol) of H_2O_2 (as a 30% solution in H_2O), 0.5 g of TS-1 pellets, 50 g methanol and a CO_2 pressure of 88 bar for 1 hour at 40°C.

The reaction resulted in 94% selectivity for the epoxide compared with a selectivity of 59% without the use of carbon dioxide.

Example 6

The general procedure of example 1 was repeated using a propylene feedstock in place of the 1-octene

In the reaction the following proportions and conditions were used: 2.47 g (58.3 mmol) of propylene, 0.656 g (5.8 mmol) of H_2O_2 (as a 30% solution in H_2O), 0.5 g of TS-1 pellets, 50 g methanol and a CO_2 pressure of 88 bar for 1 hour at 40°C.

The reaction resulted in 100% selectivity for the epoxide compared with a selectivity of 87% without the use of

carbon dioxide.

Example 7

A series of experiments were undertaken using the general procedure of Example 3 at 40°C for 30 minutes, with the exception that for some of the experiments the solvent to 1-octene ratio was decreased. The results are illustrated in Figure 5. These results show that even at low ratios of solvent to substrate the epoxide selectivity and oxidant conversion both remain high.

Claims

1. A process for the conversion of one or more unsaturated hydrocarbons to one or more oxidation products which process comprises reacting one or more unsaturated hydrocarbons in a reaction mixture under oxidation conditions in the presence of an oxidant, a heterogeneous catalyst and a solvent characterised in that the catalyst comprises a Group IVB, VB or VIB metal and that carbon dioxide is present in the reaction mixture.

2. A process as claimed in claim 1 wherein the catalyst is a metal molecular sieve.

3. A process as claimed in claim 1 or claim 2 wherein the metal is a Group IVB metal.

4. A process as claimed in claim 3 wherein the metal is titanium.

5 A process as claimed in any one of claims 1 to 4 wherein the solvent is methanol.

6. A process as claimed in any of the preceding claims wherein the oxidant is hydrogen peroxide.

7. A process as claimed in any one of the preceding claims wherein the unsaturated hydrocarbon is an olefin.

8. A process as claimed in any of the preceding claims wherein the carbon dioxide is present under supercritical conditions.

9. A process as claimed in any of the preceding claims

wherein the oxidation product is one or more epoxides.

10. A process as claimed in any of claims 1 to 8 wherein the oxidation product is one or more aldehydes, ketones or acids.

11. A process as claimed in claim 9 comprising an additional step wherein the epoxide is converted to one or more acids or alcohols.

12. A process as claimed in claim 11 wherein the one or more acids or alcohols are linear acids and linear alcohols.

13. A process as claimed in any of the preceding claims wherein the ratio of solvent to unsaturated hydrocarbon is less than 8:1.

14. A process as claimed in claim 13 wherein the ratio is 1:1 or less.

15. A process as claimed in any of the preceding claims wherein the reaction mixture comprises at least 1% by weight of carbon dioxide.

16. A process as claimed in claim 15 wherein the reaction mixture comprises at least 25% by weight of carbon dioxide.

17. A process as claimed in any of the preceding claims wherein the carbon dioxide constitutes more than 50% by weight of the solvent used in the reaction mixture.

18. A process according to any one of claims 4 to 17 wherein the catalyst is selected from one of the

following: TS-1, TS-2, TS-3, titanium zeolite beta, TS-48, titanium mordenite and titanium silicalite.

19. A process according to any of claims 1 to 18 wherein the reaction residence time is at least 20% less than that required to achieve 50% conversion without the presence of carbon dioxide.

20. A process according to claim 19 wherein the reaction residence time is at least 50% less.

21. A process according to either claim 20 or claim 21 wherein the conversion is 90%.

22. A process as claimed in any of the preceding claims wherein the reaction pressure is between 1 and 700 atmospheres.

23. A process as claimed in any of the preceding claims wherein the epoxidation reaction temperature is from 0°C to 100°C.

24. A process as claimed in claim 23 wherein the reaction temperature is within the range 40°C to 80°C.

25. A process as claimed in any of the preceding claims wherein the reaction residence time is within the range 10 minutes to 48 hours.

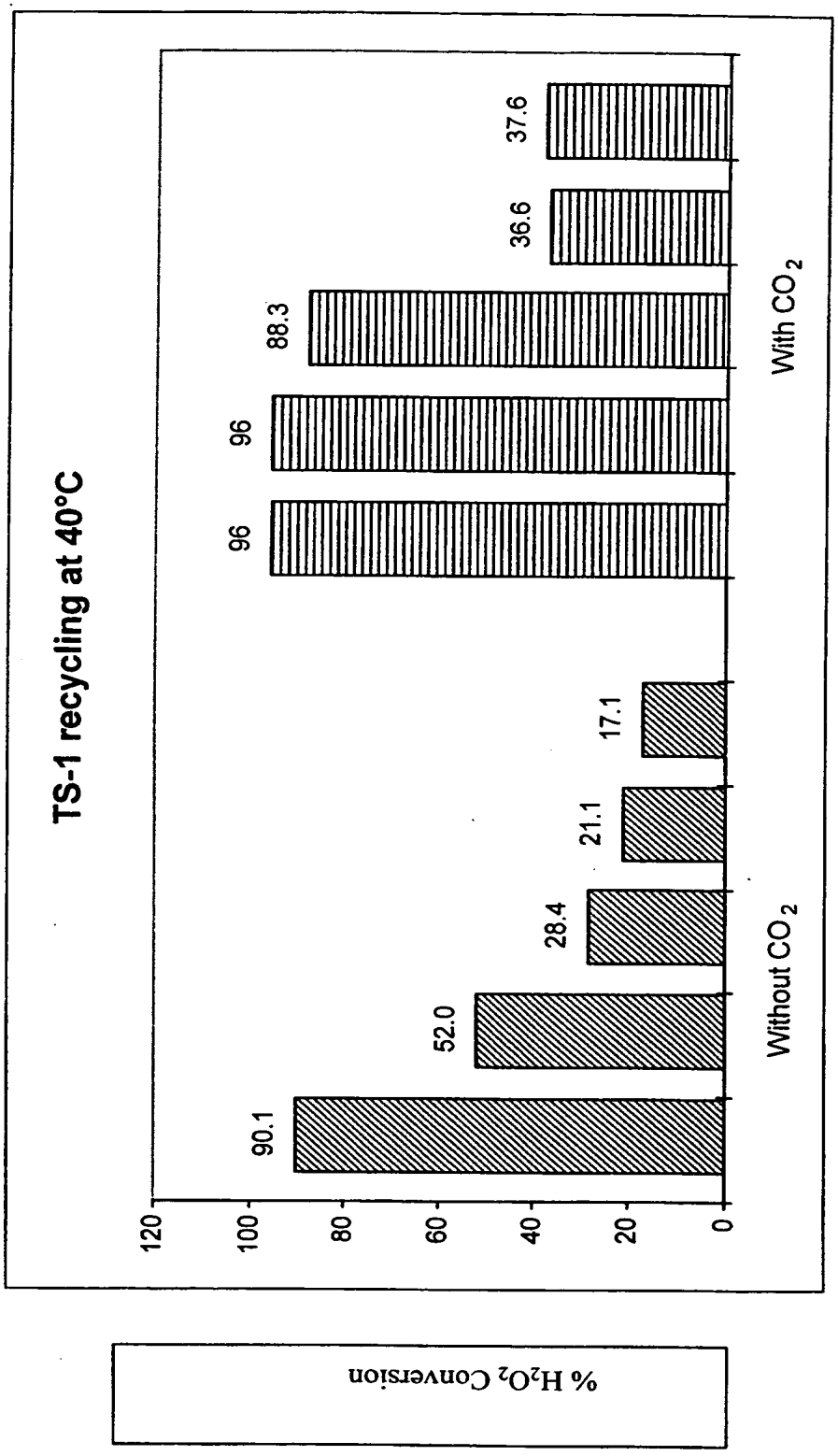

TS-1 recycling at 40°C
% H_2O_2 Conversion
120
100
80
60
40
20
0
90.1
52.0
28.4
21.1
17.1
96
96
88.3
36.6
37.6
Without CO_2
With CO_2

Fig 1

Fig 2

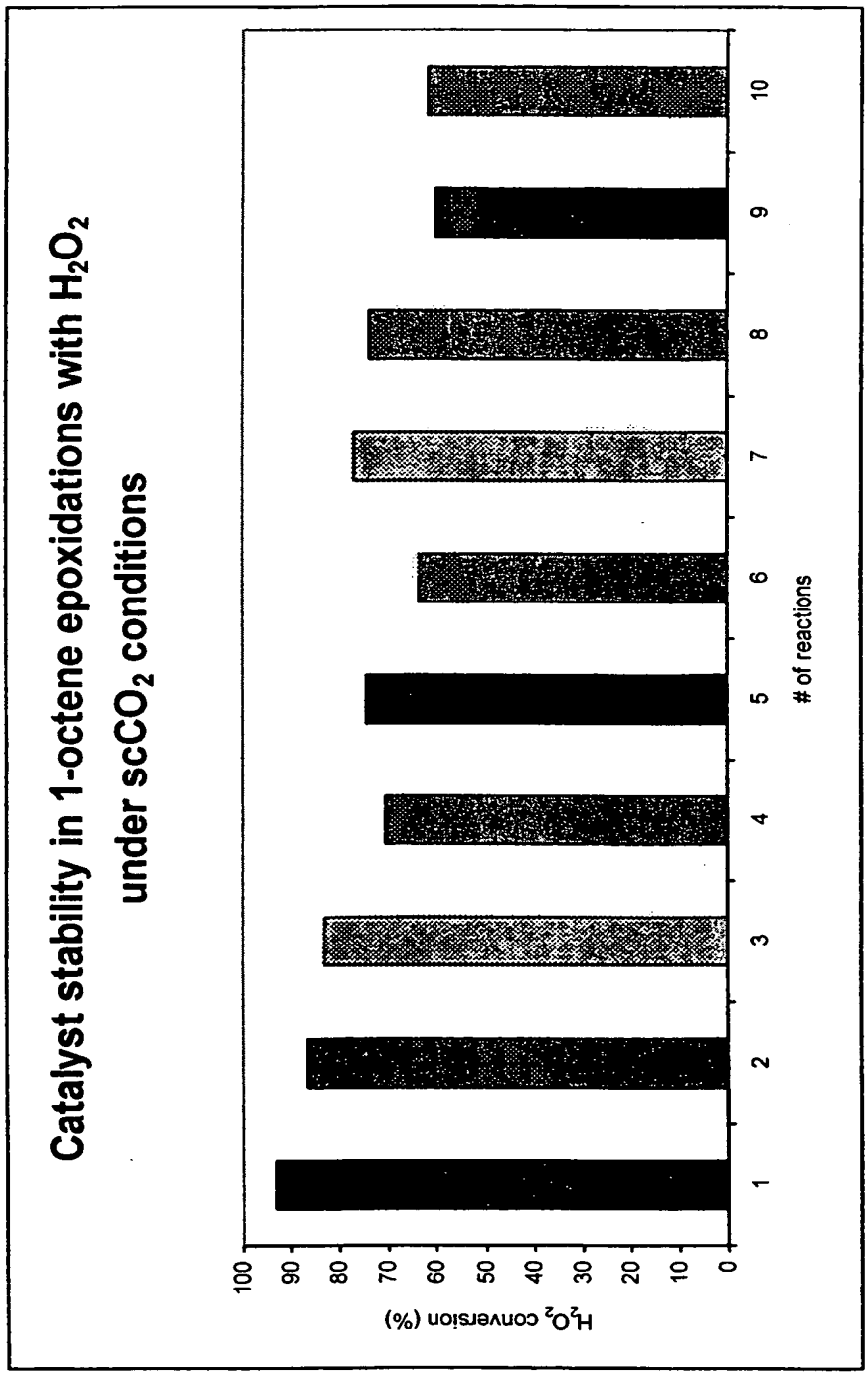
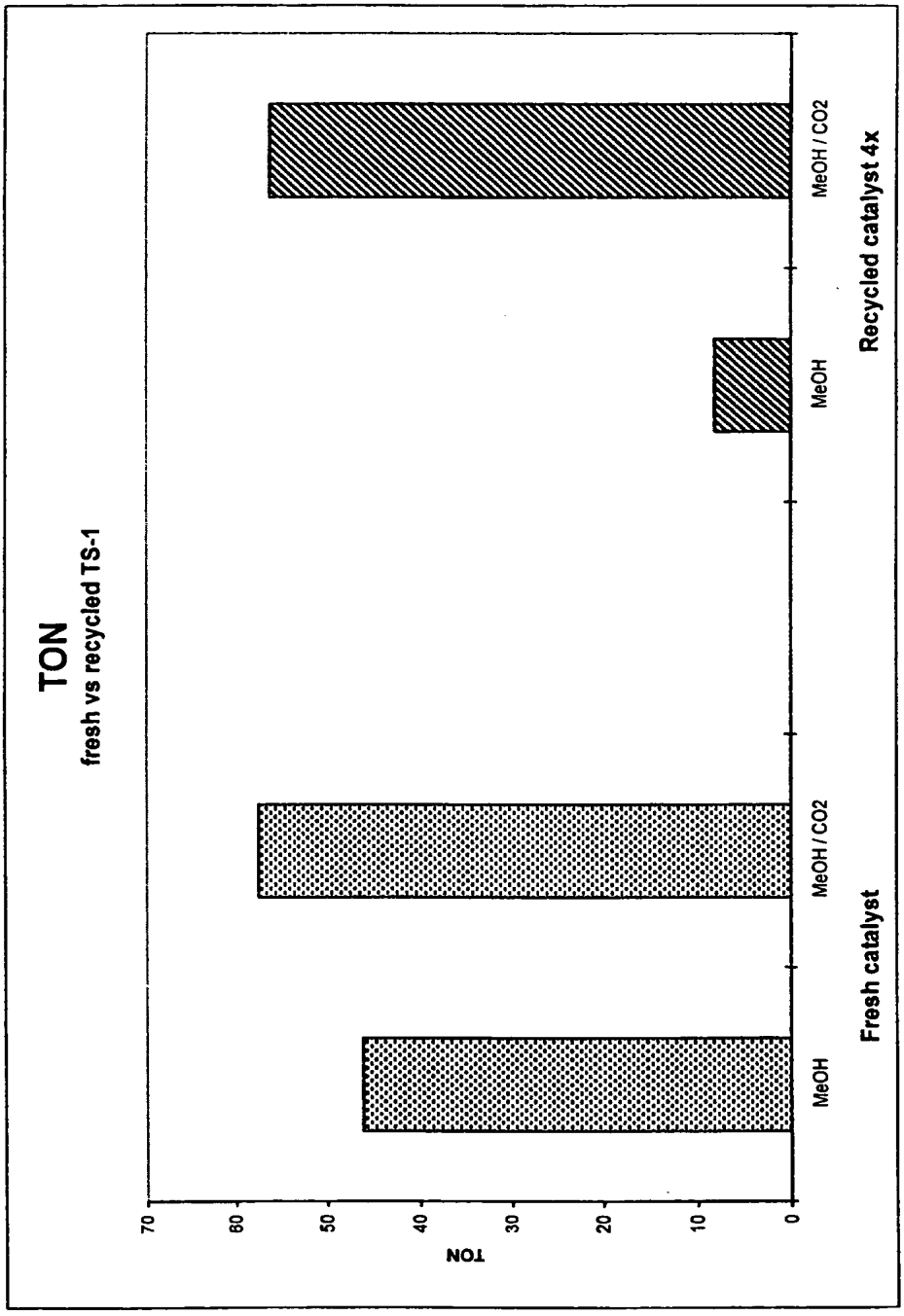

Catalyst stability in 1-octene epoxidations with H_2O_2 under $scCO_2$ conditions
H_2O_2 conversion (%)
0
10
20
30
40
50
60
70
80
90
100
1
2
3
4
5
6
7
8
9
10
of reactions

Fig 3


TON
fresh vs recycled TS-1
TON
70
60
50
40
30
20
10
0
MeOH
MeOH / CO2
MeOH
MeOH / CO2
Fresh catalyst
Recycled catalyst 4x

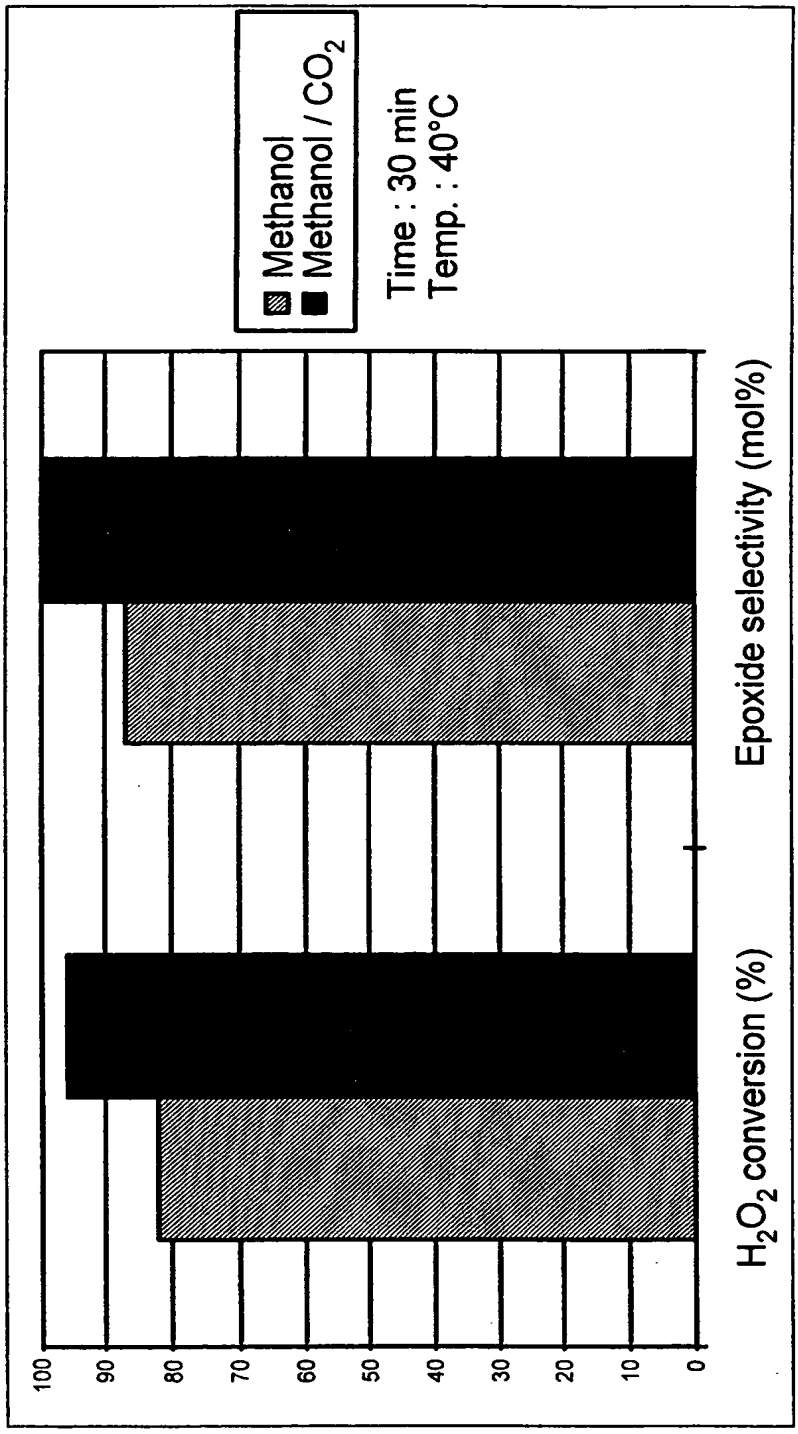

Methanol
Methanol / CO_2
Time : 30 min
Temp. : 40°C
H_2O_2 conversion (%)
Epoxide selectivity (mol%)
100
90
80
70
60
50
40
30
20
10
0

Fig 4

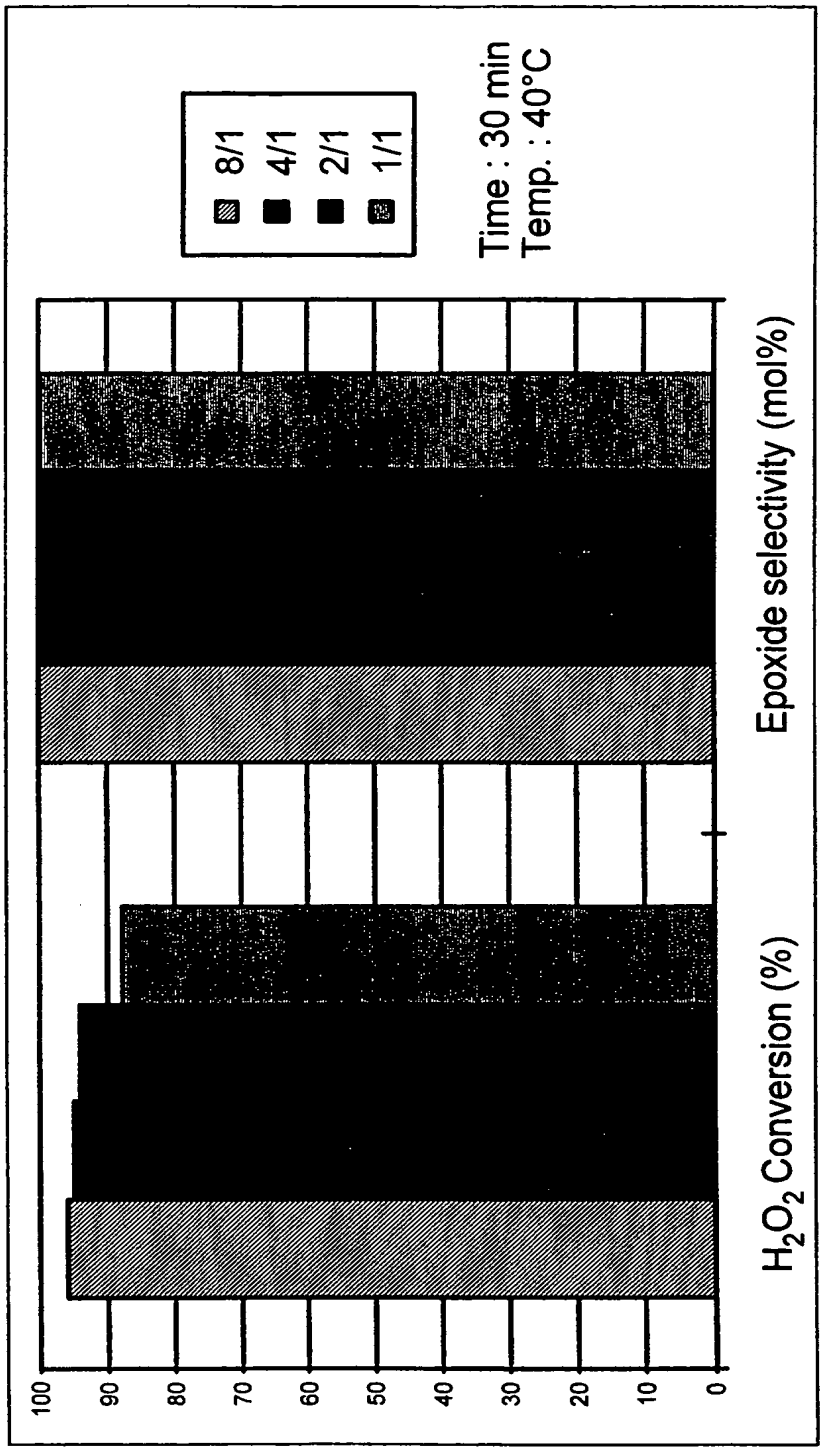

8/1
4/1
2/1
1/1
Time : 30 min
Temp. : 40°C
Epoxide selectivity (mol%)
H_2O_2 Conversion (%)
100
90
80
70
60
50
40
30
20
10
0

Fig 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03998

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07B33/00 C07D301/12 C07C27/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D C07B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 196 00 709 A (BASF AG) 17 July 1997 (1997-07-17) the whole document, particularly column 5, lines 31-49	1-25
Y	US 5 210 336 A (GAFFNEY A M ET AL) 11 May 1993 (1993-05-11) cited in the application the whole document	1-25
Y	US 4 833 260 A (NERI C ET AL) 23 May 1989 (1989-05-23) cited in the application the whole document	1-25
P,X	DE 197 25 820 A (LINDE AG) 24 December 1998 (1998-12-24) the whole document, particularly claim 4	1-25

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 September 1999	15/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Allard, M

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03998

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DE 197 23 949 A (BASF AG) 10 December 1998 (1998-12-10) the whole document, particularly column 12 lines 16-19 in combination with lines 44 and 45	1-25
A	US 4 483 996 A (JACOBSON S E) 20 November 1984 (1984-11-20) cited in the application	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/03998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19600709 A	17-07-1997	NONE	
US 5210336 A	11-05-1993	EP 0385631 A	05-09-1990
		JP 2264734 A	29-10-1990
US 4833260 A	23-05-1989	IT 1152299 B	31-12-1986
		AT 21896 T	15-09-1986
		CA 1196925 A	19-11-1985
		DK 341483 A	29-01-1984
		EP 0100119 A	08-02-1984
		JP 1721832 C	24-12-1992
		JP 4005028 B	30-01-1992
		JP 59051273 A	24-03-1984
DE 19725820 A	24-12-1998	NONE	
DE 19723949 A	10-12-1998	AU 8214098 A	21-12-1998
		WO 9855228 A	10-12-1998
US 4483996 A	20-11-1984	EP 0117147 A	29-08-1984
		JP 59163334 A	14-09-1984

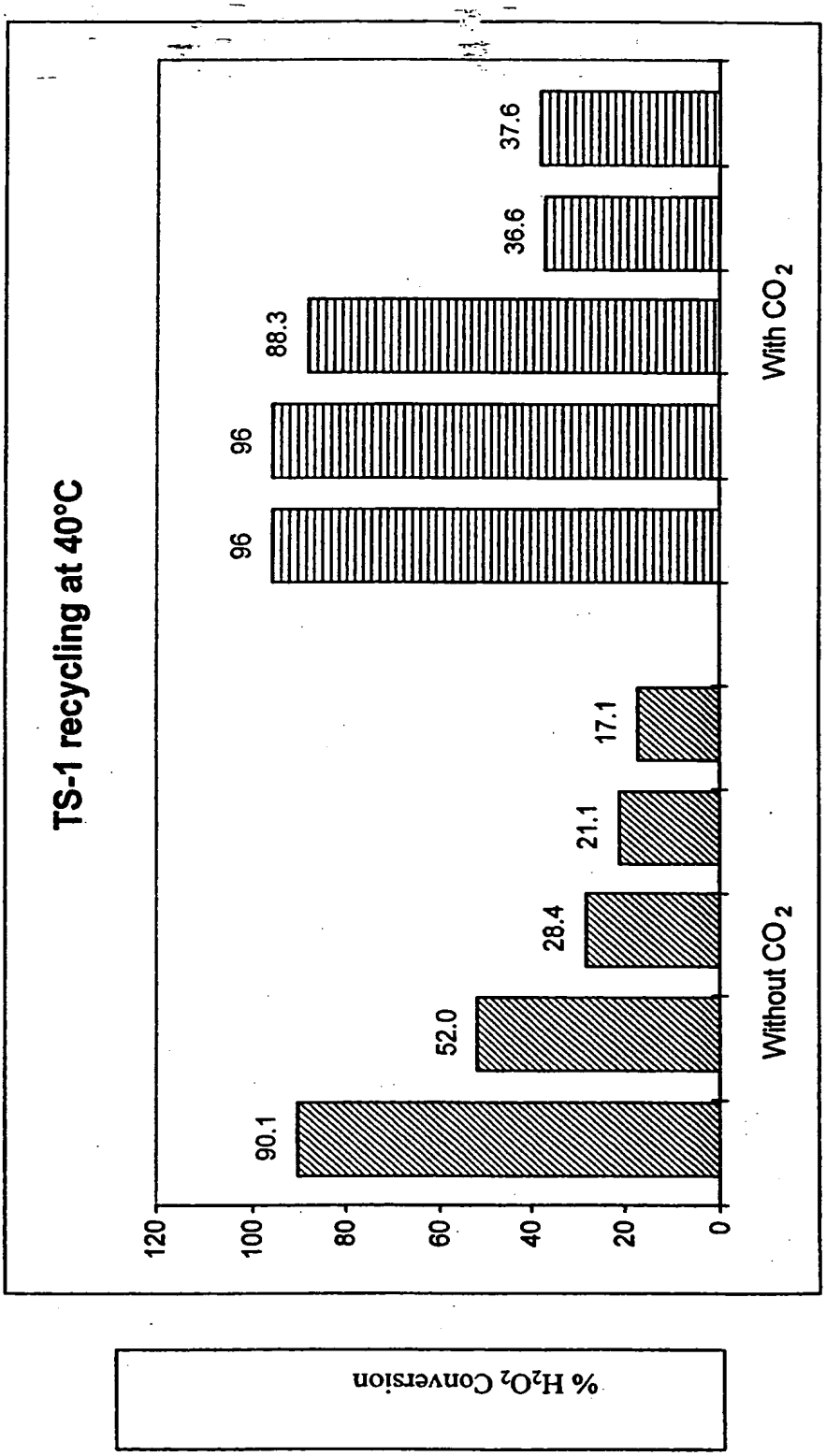

TS-1 recycling at 40°C
% H_2O_2 Conversion
120
100
80
60
40
20
0
90.1
52.0
28.4
21.1
17.1
96
96
88.3
36.6
37.6
Without CO_2
With CO_2

Fig 1

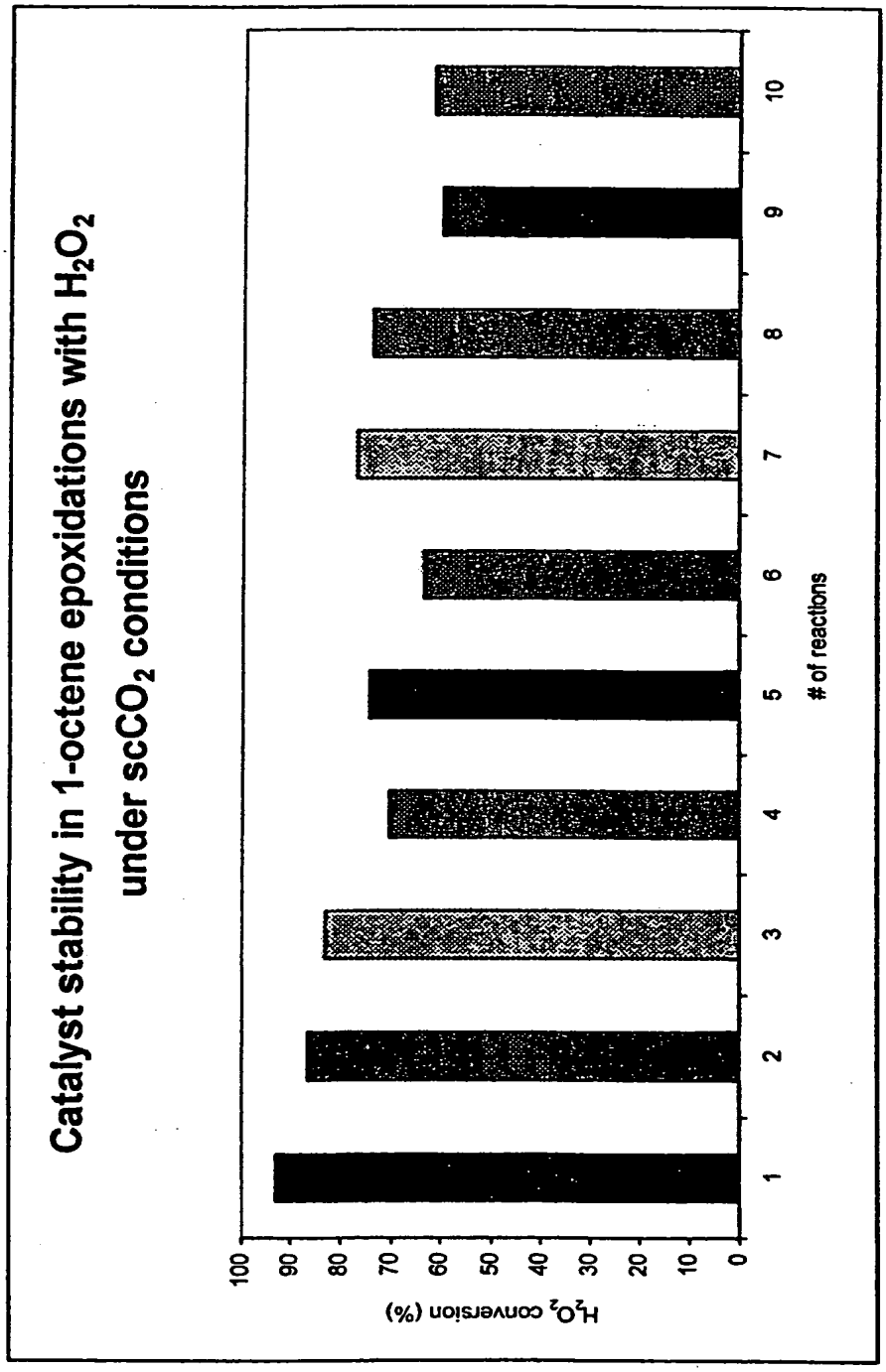


Fig 2

SUBSTITUTE SHEET (RULE 26)

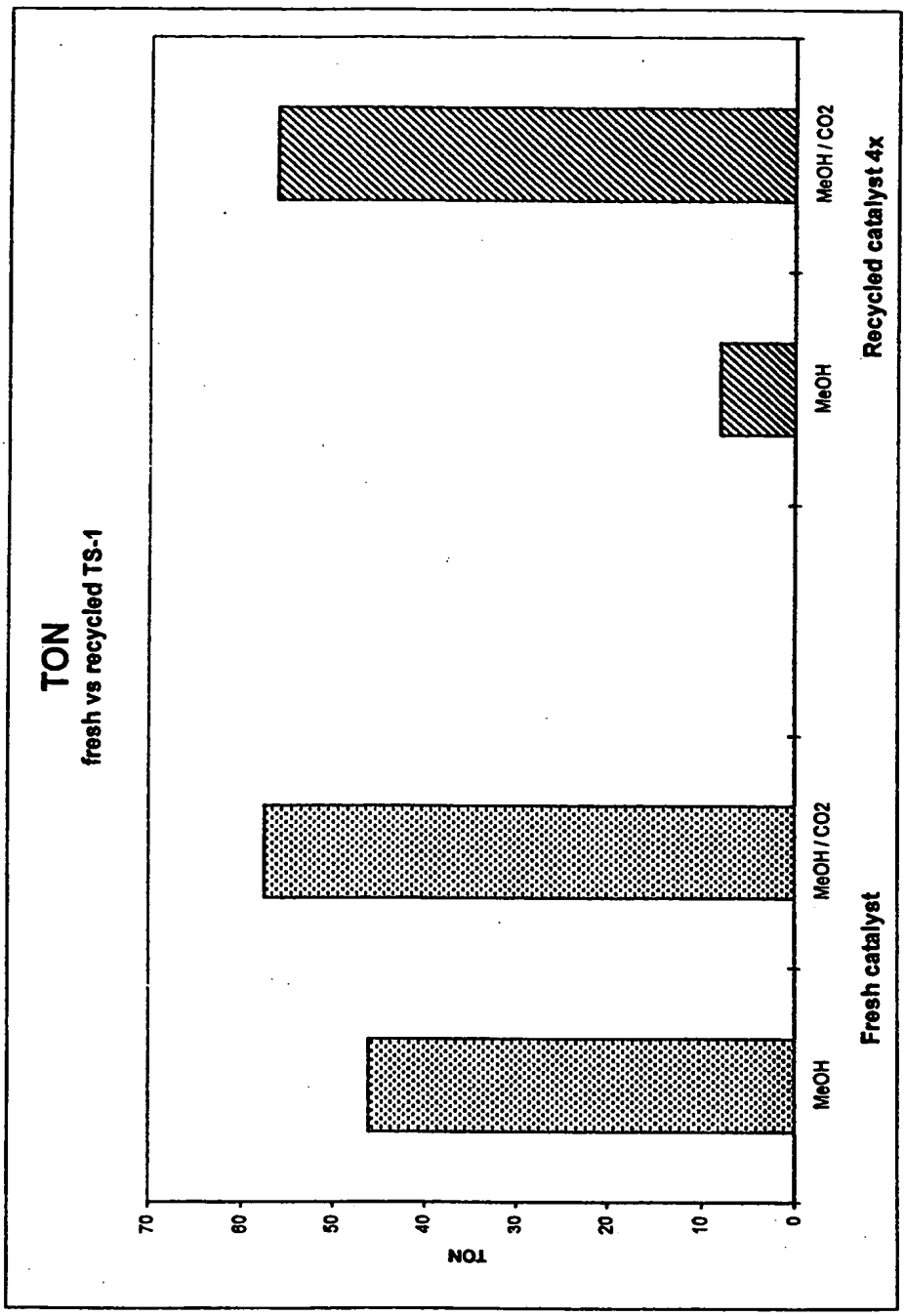


Fig 3

SUBSTITUTE SHEET (RULE 26)

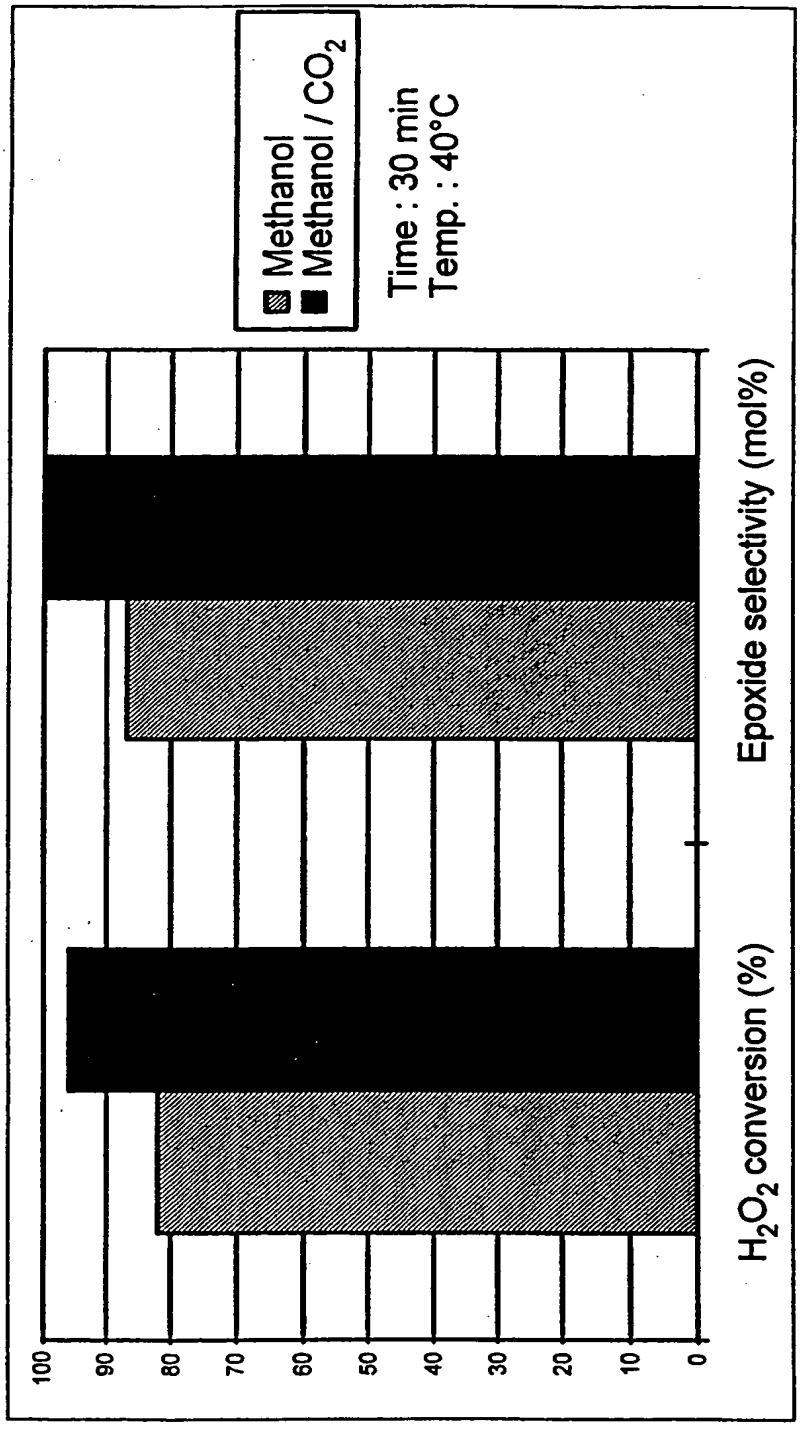

Methanol
Methanol / CO_2
Time : 30 min
Temp. : 40°C
Epoxide selectivity (mol%)
H_2O_2 conversion (%)
100
90
80
70
60
50
40
30
20
10
0

Fig 4

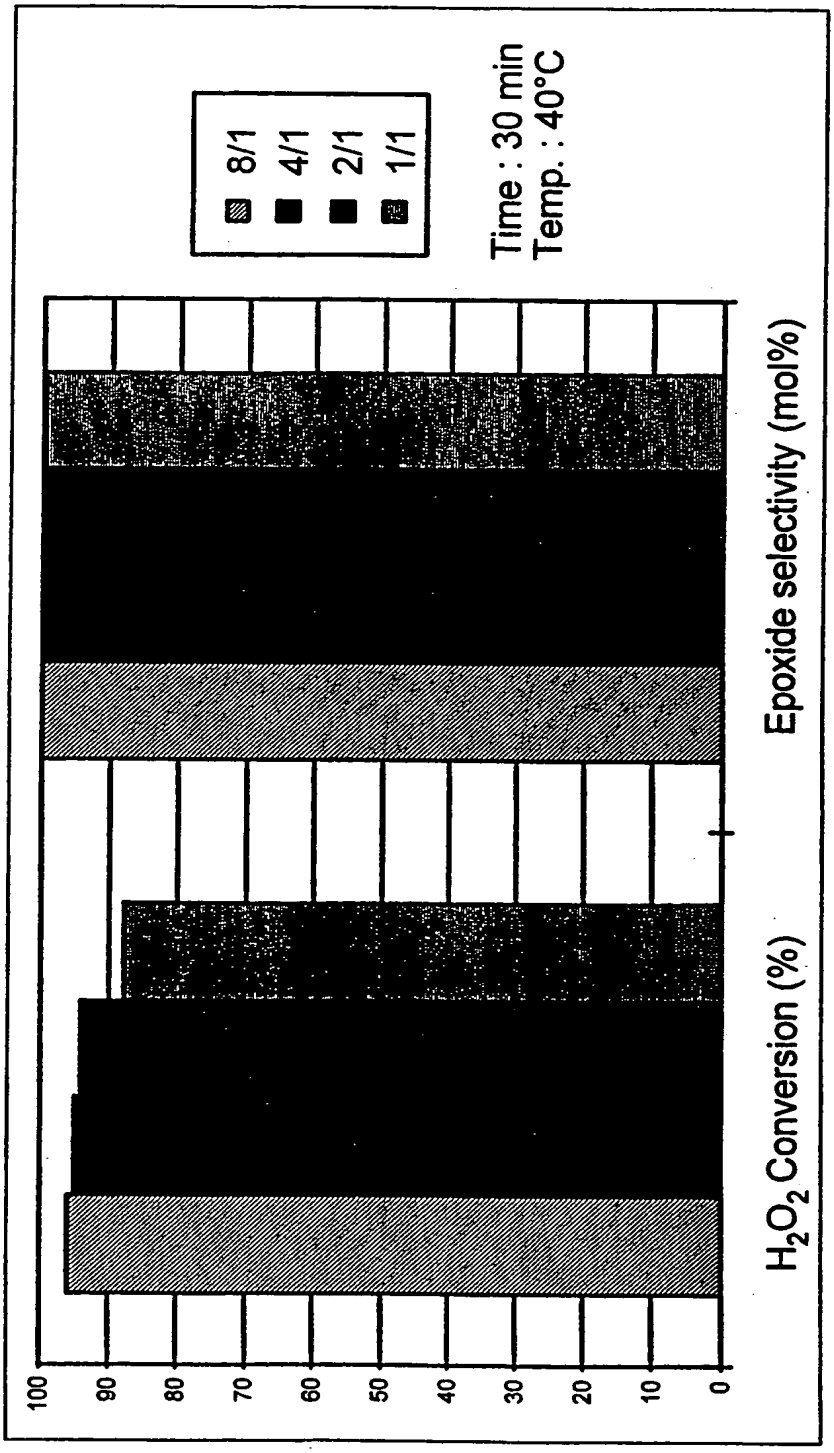

8/1
4/1
2/1
1/1
Time : 30 min
Temp. : 40°C
Epoxide selectivity (mol%)
H_2O_2 Conversion (%)
100
90
80
70
60
50
40
30
20
10
0

Fig 5

09/719375
05 Rec'd PCT/PTO 0 8 DEC 2000

S/PRTS

Oxidation Process

The present invention relates to an oxidation process and in particular to a process for the oxidation of unsaturated hydrocarbons in the presence of catalyst under heterogeneous conditions.

It is well known that the epoxidation of unsaturated hydrocarbons e.g. olefinic compounds, with various oxidants such as hydrogen peroxide may be effectively catalyzed by certain synthetic zeolites containing metal atoms such as titanium atoms (see, for example, U.S. Pat. No. 4,833,260).

Various process modifications have been proposed to improve the conversion and selectivity of these oxidation reactions. U.S. Pat. No. 4,824,976 proposes that the non-selective ring-opening reactions which take place when epoxidation is performed in a protic medium such as water or alcohol may be suppressed by treating the catalyst prior to the reaction or during the reaction with a suitable acid neutralising agent. The neutralising agent is said to neutralise acid groups on the catalyst surface which tend to promote by-product formation

U.S. Pat. No. 5,675,026 proposes the addition of neutral- or acid-reactive salts to the catalyst before or during the reaction to improve catalyst activity. U.S. Pat. No. 4,483,996 discloses a process for the conversion of olefins to olefin oxides and ketones. The process utilises a thallous catalyst, with molecular oxygen as oxidant in an aqueous carbon dioxide solvent. U.S. Pat. No. 5,591,875 proposes an epoxidation process which

utilises a chelating agent to reduce the catalysts tendency to non-selectively decompose the hydrogen peroxide oxidant used. EP 0 385 631 A1 describes an oxidation process for the conversion of olefins to glycols utilising oxygen and carbon dioxide as reactants under supercritical conditions. A heterogeneous copper containing catalyst is proposed. U.S. Pat. No. 5,646,314 proposes performing the oxidation reaction in the presence of nonbasic salts in order to improve selectivity.

Furthermore it has long been recognised that metal containing zeolite catalysts rapidly become deactivated in use. There have been a number of methods developed to counter this deactivation and/or to regenerate the catalyst after use. U.S. Pat. No. 5, 741, 749 proposes a the regeneration of a titanium containing molecular sieve oxidation catalyst by treatment with a gas stream comprising specific amounts of molecular oxygen. WO 98/18555 proposes the regeneration of a titanium silicalite catalyst with a liquid solution of an oxidising agent. WO 98/ 18556 proposes the regeneration of a titanium silicalite catalyst under a specific gas flow

There are a number of problems with the processes of the prior art. Conversions and selectivities for the various reactions are in general still low or require additional process modifications which incur additional costs. Frequently the catalyst systems utilised require special treatments and/or frequent regeneration in order to maintain catalyst activity.

It has been surprisingly found that the conversion and selectivity of oxidation processes, in particular the

conversion of unsaturated hydrocarbons, especially olefins, to oxidation products especially oxirane compounds, are significantly improved by utilising a specific group of catalysts in the presence of carbon dioxide. It has also been surprisingly found that the heterogeneous catalysts of the present process maintain their activity for significantly longer periods of time and through many recycles through the process. This improved activity with respect to the catalyst means that costly and laborious pre-treatments and/or regenerations of the catalyst are either not required or are required at less frequent intervals in the process of the present invention compared to prior art processes.

Accordingly the present invention provides a process for the conversion of one or more unsaturated hydrocarbons to one or more oxidation products which process comprises reacting one or more unsaturated hydrocarbons in a reaction mixture under oxidation conditions in the presence of an oxidant, heterogeneous catalyst and a solvent characterised in that the catalyst comprises a Group IVB, VB or VIB metal and that carbon dioxide is present in the reaction mixture.

In a preferred embodiment, the present invention pertains to an epoxidation process wherein a titanium containing catalyst is utilised in the presence of hydrogen peroxide as oxidant and the carbon dioxide is present in the reaction mixture under supercritical conditions.

Suitable oxidants for the process of the present invention may be hydrogen peroxide or hydroperoxides. Examples of hydroperoxides include tert-butyl hydroperoxide (TBHP) and ethyl benzene hydroperoxide

(EBHP). The preferred oxidant for the process of the present invention is hydrogen peroxide (H_2O_2). Hydrogen peroxide (H_2O_2) utilised as the oxidant in the present invention may be obtained from any suitable source, including, for example, from autoxidation of secondary alcohols using air or other source of molecular oxygen. Suitable secondary alcohols include both aliphatic alcohols such as isopropanol and cyclohexanol as well as aromatic alcohols such as alpha methyl benzyl alcohol and anthrahydroquinones (including alkyl-substituted anthrahydroquinones). The crude reaction product thereby generated may be either used directly in the epoxidation process of this invention or, if so desired, purified, fractionated, concentrated, ion exchanged, or otherwise processed prior to such use. For example, the ketone generated as an autoxidation co-product may be separated, in whole or in part, from the hydrogen peroxide by distillation (where the ketone is relatively volatile) or by extraction with water (where the ketone is substantially immiscible with or insoluble in water). The hydrogen peroxide may alternatively be generated in situ by, for example, combining oxygen, secondary alcohol, olefin, and catalyst within a reaction zone under conditions effective to accomplish simultaneous secondary alcohol autoxidation and olefin epoxidation. Generally speaking, it will be desirable to employ initial hydrogen peroxide concentrations of from about 1 to 20 weight per cent in the liquid phase within the reaction zone.

The unsaturated hydrocarbon is preferably an organic compound having from two to thirty carbon atoms and at least one ethylenically unsaturated functional group (i.e. a carbon-carbon double bond) and may be a cyclic, branched or straight chain aliphatic olefin. More than

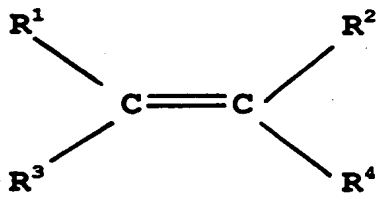
one carbon-carbon double bond may be present in the olefin, dienes, trienes, and other polyunsaturated substrates thus may be used.

Exemplary olefins suitable for use in the process of this invention include ethylene, propylene, the butenes, butadiene, the pentenes, isoprene, hexenes, heptenes, octenes, diisobutylene, nonenes, the trimers and tetramers of propylene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclooctadiene, dicyclopentadiene, methylenecyclopropane, methylenecyclopentane, methylenecyclohexane, vinylcyclohexane, and vinyl cyclohexene. Preferred olefins are 1-octene, propylene and cyclopentene.

Mixtures of olefins may be epoxidized and resulting mixture of epoxides either employed in mixed form or separated into the different component epoxides. One example of a preferred olefin mixture is a raffinate mixture which comprises mixed butenes; 1-butene, cis-2-butene, trans-2-butene and iso-butene.

The resulting epoxide or epoxide mixture may be rearranged to the corresponding linear aldehyde or ketone, either in-situ or in a separate step. Subsequent oxidation or hydrogenation of the aldehyde will result in the corresponding linear acid or linear alcohol. Subsequent hydrogenation of the ketone wil result in secondary alcohols.

The process of this invention is especially useful for the epoxidation of C_2-C_{10} olefins having the general structure:



wherein R^1, R^2, R^3, and R^4 are the same or different and are selected from the group consisting of hydrogen and C_1-C_8 alkyl (selected so that the total number of carbons in the olefin does not exceed 30).

The process of this invention is also suitable for use in epoxidizing olefins containing functional groups other than aliphatic hydrocarbyl moieties. For example, the carbon-carbon double bond can be substituted with groups such as $-CO_2H$, $-CO_2R_1$, -CN, or -OR wherein R is an alkyl, cycloalkyl, aryl or aralkyl substituent. The radicals R^1, R^2, R^3, and R^4 in the structural formula shown hereinabove may contain aryl, aralkyl, halo, nitro, sulfonic, cyano, carbonyl, (e.g. ketone, aldehyde,) hydroxyl, carboxyl (e.g ester, acid) or ether groups. Examples of olefins of these types include allyl alcohol, styrene, allyl chloride, allyl methyl ether, allyl phenyl ether, methyl methacrylate, acrylic acid, methyl acrylate, stilbene, and the like.

The amount of hydrogen peroxide relative to the

amount of olefin is not critical, but most suitably the molar ratio of olefin: hydrogen peroxide is from about 100:1 to 1:10 when the olefin contains one ethylenically unsaturated group. The molar ratio of ethylenically unsaturated groups in the olefin to hydrogen peroxide is more preferably in the range of from 1:2 to 10:1.

The heterogeneous catalysts contain a Group IVB (e.g. Ti, Zr or Hf), VB (e.g. V, Nb or Ta) or VIB (e.g. Cr, Mo or W) metal and may be crystalline and/or amorphous. The most preferred catalysts contain a Group IVB metal. Particularly preferred catalysts are crystalline molecular sieves especially zeolites which contain titanium.

The titanium silicalites useful as catalysts in the epoxidation step of the process comprise the class of zeolite substances wherein titanium is substituted for a portion of the silicon atoms in the lattice framework of a molecular sieve. Such substances are well-known in the art.

Particularly preferred titanium silicalites include the classes of molecular sieves commonly referred to as "TS-1" (having an MFI topology analogous to that of the ZSM-5 aluminosilicate zeolites), "TS-2" (having an MEL topology analogous to that of the ZSM-11 aluminosilicate zeolites), and "TS-3" (as described in Belgian Pat. No. 1,001,038). Also suitable are the titanium-containing molecular sieves having framework structures isomorphous to zeolite beta. Also suitable is TS-48 with the structure of zeolite ZSM-48 as well as titanium mordenite with the MOR structure. The titanium silicalite preferably contains no non-oxygen elements other than titanium and silica in the lattice framework, although

minor amounts of boron, iron, aluminum, and the like may be present.

Titanium silicalite catalysts suitable for use in the process of this invention will generally have a composition corresponding to the following empirical formula $xTiO_2:(1-x)SiO_2$, where x is between 0.0001 and 0.500. More preferably, the value of x is from 0.01 to 0.125. The molar ratio of Si:Ti in the lattice framework of the titanium silicalite is advantageously from 9.5:1 to 99:1 (most preferably, from 9.5:1 to 60:1). The use of relatively titanium-rich silicalites may also be desirable. The preferred catalyst is titanium silicalite-1. One form of catalyst suitable for use in the process of the present invention is a "cherry type" catalyst which consists of a core of material e.g. silica/alumina and a shell of different material e.g. silica/titania as described for example in EP 634 212. The titanium silicalite catalyst may be incorporated in or in the form of a membrane; for example TS-1 or Ti-MCM-41 may be occluded in polydimethylsiloxane (PDMS) membranes, as described in Chemical Communications (1997) pages 137 to 138.

The amount of catalyst employed is not critical, but should be sufficient so as to substantially accomplish the desired epoxidation reaction in a particularly short period of time. The optimum quantity of catalyst will depend upon a number of factors including reaction temperature, olefin reactivity and concentration, hydrogen peroxide concentration, type and concentration of organic solvent as well as catalyst activity and the type of reactor or reaction system (i.e. batch vs continuous) employed. In a batch-type or slurry reaction, for example, the amount of catalyst will

typically be from 0.001 to 10 grams per mole of olefin. In a fixed or packed bed system, the optimum quantity of catalyst will be influenced by the flow rate of reactants through the fixed bed; typically, from about 0.05 to 2.0 kilograms hydrogen peroxide per kilogram catalyst per hour will be utilised. The concentration of titanium in the liquid phase reaction mixture will generally be from about 10 to 10,000 ppm.

The catalyst may be utilised in powder, pellet, microspheric, extruded, monolithic or any other suitable physical form. The use of a binder (co-gel) or support in combination with the titanium silicalite may be advantageous. Supported or bound catalysts may be prepared by the methods known in the art to be effective for zeolite catalysts in general. Preferably, the binder or support is essentially non-acidic and does not catalyze the non-selective decomposition of hydrogen peroxide or ring-opening of the epoxide. Two or more heterogeneous catalysts may be used if desired.

Illustrative binders and supports include titania, silica, alumina, silica-alumina, silica-titania, silica-thoria, silica-magnesia, silica-zirconia, silica-beryllia, and ternary compositions of silica with other refractory oxides. Also useful are clays such as montmorillonites, koalins, bentonites, halloysites, dickites, nacrites, and ananxites. The proportion of titanium silicalite binder or support may range from 99:1 to 1:99, but preferably is from 5:95 to 80:20.

The epoxidation reaction temperature is preferably from 0°C to 100°C (more preferably from 40°C to 80°C), which has been found to be sufficient to accomplish selective conversion of the olefin to epoxide within a

reasonably short period of time with minimal non-selective decomposition of the hydrogen peroxide. It is generally advantageous to carry out the reaction to achieve as high a hydrogen peroxide conversion as possible, preferably at least 50%, more preferably at least 90%, most preferably at least 99%, consistent with high selectivities. The optimum reaction temperature will be influenced by catalyst concentration and activity, substrate reactivity, reactant concentrations and type of solvent employed, amongst other factors.

Reaction or residence times of from about 10 minutes to 48 hours will typically be appropriate, depending upon the above-identified variables. One advantage of the present invention however is that the reaction time required to achieve near quantitative conversion of the oxidant may be considerably shorter compared with those reactions undertaken in the absence of CO_2. This reduction in reaction time may be as much as 20% or even 50% or more. Thus the reaction residence time is at least 20% less and more preferably at least 50% less, than that required for 50%, more preferably 90% and most preferably 99% conversion of the oxidant, in a reaction without the presence of carbon dioxide.

The reaction is performed at elevated pressure (typically, between 1 and 700 atmospheres). Generally, it will be desirable to maintain the reaction components as a liquid mixture. For example, when an olefin such as propylene is used having a boiling point at atmospheric pressure which is less than the epoxidation temperature, a superatmospheric pressure sufficient to maintain the desired concentration of propylene in the liquid phase is preferably utilised.

The epoxidation process of this invention may be

carried out in a batch, continuous, or semi-continuous manner using any appropriate type of reaction vessel or apparatus such as a fixed bed, transport bed, stirred slurry, or CSTR reactor. Known methods of conducting metal-catalysed epoxidations using hydrogen peroxide will generally also be suitable for use. Thus, the reactants may be combined all at once or sequentially. For example, the hydrogen peroxide and/or the olefin may be added incrementally to the reaction zone.

The oxidation must be carried out in the presence of carbon dioxide in the gaseous, liquid or supercritical state. It is most preferred that the carbon dioxide is present in the supercritical state which is where it exists as a one phase fluid occurring above both a critical temperature and pressure Tc and Pc, which is 31°C and 73.8 kg/cm^2. The reaction mixture including catalyst comprises at least 1% by weight of carbon dioxide, preferably at least 10% by weight and more preferably at least 25% by weight of the reaction mixture including catalyst. In a most preferred embodiment the carbon dioxide constitutes more than 50% by weight of the solvent used in the reaction mixture.

Any solvent or combination of solvents which are compatible with carbon dioxide may be used. The preferred solvent has methanol as its main constituent in combination with carbon dioxide. Other suitable solvents include, but are not limited to water alcohols (especially C_1-C_{10} aliphatic alcohols such as isopropanol), ketones (especially C_3-C_{10} ketones such as acetone), and mixtures of such solvents. It is preferred that supercritical carbon dioxide is present as the solvent or in admixture with other solvents. Accordingly carbon dioxide when present as a solvent should be at

least 1% by weight of the solvent mixture and preferably at least 5 to 100%, most preferably 25 to 100% by weight of the solvent. In a most preferred embodiment the carbon dioxide comprises at least 50% by weight of the solvent. The total amount of solvent in the reaction mixture will depend on a number of factors including the nature of the substrate being oxidised, the form and nature of introduction of the oxidant and the amount of CO_2 present. It has surprisingly been found that in the process of the present invention the ratio of solvent to substrate (unsaturated hydrocarbon or hydrocarbons being oxidised) may be significantly less than that required using the typical reaction conditions described in the art. This has the benefit of either enabling the reactor capacity to be better utilised or to enable the economic use of smaller reactors. In addition the requirement for less solvent results in less solvent recycle and a more energy efficient process. Typically reaction conditions in the art require solvent to substrate ratios of 8:1 or more. In the process of the present invention it is possible to use solvent to substrate ratios of less than 8:1 preferably 7:1 or less and most preferably 4:1 or less or 2:1 or less. Solvent to substrate ratios as low as 1:1 may be used; accordingly it is preferred that the ratio is within the range of 8:1 to 1:1 and most preferably 7:1 to 1:1 or narrower ranges based on the upper limits identified. Reduction of the ratio, when using the typical reaction conditions in the art, results in inefficient utilisation of the oxidant due to unwanted side reactions. In the process of the present invention the reduction in the ratio does not have a marked detrimental effect on oxidant efficiency which is significantly maintained at even the lowest ratios.

Once the epoxidation has been carried out to the

desired degree of conversion, the epoxide product may be separated and recovered from the reaction mixture using any appropriate technique such as fractional distillation, extractive distillation, liquid-liquid extraction, crystallisation, or the like. After separating from the epoxidation reaction mixture by any suitable method such as filtration (as when a slurry reactor is utilised, for example), the recovered titanium silicalite catalyst may be economically re-used in subsequent epoxidations. Where the catalyst is deployed in the form of a fixed bed, the epoxidation product withdrawn as a stream from the epoxidation zone will be essentially catalyst free with the catalyst being retained within the epoxidation zone. Similarly, any unreacted olefin or hydrogen peroxide may be separated and recycled or otherwise disposed of. In certain embodiments of the instant process where the epoxide is produced on a continuous basis, it may be desirable to periodically or constantly regenerate all or a portion of the used catalyst in order to maintain optimum activity and selectivity. Suitable regeneration techniques are well-known and include, for example, calcination and solvent treatment. Such regeneration and/or treatment may not be necessary until a significant number of recycles have occurred through the process of the present invention. Typical examples of suitable regeneration methods are provided in WO99/01445, WO98/18556, WO98/28072 and Journal of Molecular Catalysis A:Chemical 117 (1997) 351-356. The disclosures of each of these references are incorporated by reference.

From the foregoing description, one skilled in the art can readily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof can make various changes and

modifications of the invention to adapt it to various usages, conditions, and embodiments.

The present invention is further illustrated by means of the following examples:

Example 1

A TS-1 catalyst (prepared by the procedure given in Applied Catalysis, 99, (1993), pages 71-84) was utilised in the oxidation of 1-octene to 1,2-epoxyoctane with and without supercritical carbon dioxide as the solvent. A 250 cm^3 batch autoclave equipped with a temperature controller, mechanical stirrer (1000 rpm), reagents feed line, sampling line and vent line was charged in two separate experiments with the following reagents.

Reagents	Experiment 1	Experiment 2
	Weight (g)	Weight (g)
1-octene	14.52	7.26
H_2O_2 (30wt% in H_2O)	0.44*	0.22*
Methanol	112.5	56.25
Carbon Dioxide	0	74.2
TS-1 catalyst	1.0	0.5
Total	128.46	138.43

*= the weight of H_2O_2 does not include the weight of H_2O

For Experiment 1 the reaction was undertaken at 65°C for 60 minutes. For Experiment 2 the reactor was first pressurised with carbon dioxide gas to 48 bar (48 x 10^5 Nm^{-2}), after which 74.2g of liquid carbon dioxide was

added. The reaction was undertaken at 65°C for 60 minutes and at a pressure of 106 bar (106 x 10^5 Nm^{-2}). The composition of the reaction mixtures was determined using Gas Chromatography and the hydrogen peroxide content was determined using iodometric titration.

The results are provided in Table 1.

Table 1

Experiment	Mole % 1,2-epoxyoctane	Mole % Glycolethers	% Conversion of H_2O_2
1	77.8	22.2	97.9
2	91.1	8.9	98

It can be seen from the above results that for a given conversion the selectivity is greatly enhanced when carbon dioxide is used in the oxidation utilising TS-1 as catalyst.

Example 2

In a further set of experiments the solvent system utilised was methanol or methanol/CO_2 under supercritical conditions.

In a first set of experiments (Experiment 3) the TS-1 catalyst was used in a methanol solvent and recycled without treatment or regeneration. In a second set of experiments (Experiment 4) the TS-1 catalyst was used in a methanol/carbon dioxide solvent system under supercritical conditions with respect to the carbon dioxide again the catalyst was recycled without further treatment or regeneration.

Methanol Solvent - Catalyst Recycle

The following reagents were used:

Reagents	Experiment 3
	Weight (g)
1-octene	7.26
H_2O_2 (30wt% in H_2O)	0.22*
Methanol	56.3
Carbon Dioxide	0
TS-1 catalyst	0.5
Total	64.23

*= the weight of H_2O_2 does not include the weight of H_2O

The reaction was undertaken at 40°C for 60 minutes in a 100 cm^3 glass reactor with magnetic stirrer and chilled water cooler on an electrical heating mantle. On completion the reactor was recharged with reagents and the used catalyst was recycled by filtration and drying in vacuo at room temperature for 10 minutes. The catalyst was recycled four times and the results are provided in Table 2.

EP 0 933 363 A1

Table 2			
Run Number	Mole % 1,2-epoxyoctane	Mole % Glycolethers	%Conversion of H_2O_2
1.Fresh catalyst	89.5	10.5	90.1
2.First recycle	100	0	52.0
3.Second recycle	100	0	28.4
4.Third recycle	100	0	21.1
5.Fourth recycle	100	0	17.1

It can be seen from the results in Table 2 that the conversion of hydrogen peroxide is dramatically reduced on recycling the catalyst.

Methanol Solvent with Carbon Dioxide - Catalyst Recycle

The following reagents were used:

Reagents	Experiment 4
	Weight (g)
1-octene	7.26
H_2O_2 (30wt% in H_2O)	0.22*
Methanol	56.25
Carbon Dioxide	82.8
TS-1 catalyst	0.5
Total	147.03

*= the weight of H_2O_2 does not include the weight of H_2O

A 250 cm^3 batch autoclave equipped with a temperature controller, mechanical stirrer, reagents feed line, sampling line and vent line was filled with all the above reagents except carbon dioxide and 1-octene. Then the reactor was pressurised with carbon dioxide gas to 52 bar (52 x 10^5 Nm^{-2}), after which 82.6g of liquid carbon dioxide was added, then 1-octene was injected and the reaction was undertaken at 40°C for 30 minutes and at a pressure of 74.3 bar (74.3 x 10^5 Nm^{-2}). On completion of the reaction the catalyst was removed by filtration and dried in air before being twice recycled using the same reactor, reagents and conditions. The results are provided in Table 3.

Table 3

Run Number	Mole % 1,2-epoxyoctane	Mole % Glycolether	%Conversion of H2O2
1.Fresh catalyst	100	0	96
2.First recycle	100	0	96
3.Second recycle	100	0	88
4.Third recycle	100	0	36.6
5.Fifth recycle	100	0	37.6

It can be seen from the results in Table 3 that utilising carbon dioxide in the reaction enables the catalyst to be recycled without a dramatic reduction in hydrogen peroxide conversion whilst maintaining a high selectivity towards the desired epoxide. The results are illustrated in Figure 1, which shows the % conversion for each recycle. Figure 2 illustrates the stability of a catalyst

in pellet form, over 10 reaction recycles, under the process conditions of experiment 4 of this example. Between 70 to 80% of the original catalyst weight was recovered at the end of the recycle. Some of the reduced conversion identified in Figures 1 and 2 is not due to catalyst deactivation but is due to catalyst losses from the reactor. Figure 3 illustrates the conversion with and without carbon dioxide using turnover number (TON). Turnover number corrects for the effects of catalyst losses from the reactor between reaction cycles and is a calculated as follows for each reaction period:

TON = mmol of epoxide / mmol of titanium in the catalyst

The results in Figure 3 show that when methanol is used as the solvent there is a dramatic reduction in catalyst effectiveness after four reaction cycles whereas when carbon dioxide is utilised according to the invention there is no significant reduction in catalyst activity after the same number of cycles.

Example 3

Example 1 was repeated with the exception that the reaction time was 30 minutes and the reaction temperature was 40°C. The results are provided in Figure 4; these results illustrate that at short reaction times and low temperature the process of the invention provides improved selectivity and oxidant conversion.

Example 4

The general procedure of example 1 experiment 2 was repeated using a raffinate-2 feedstock in place of the 1-octene. The raffinate-2 feedstock comprised 29.9 wt% of 1-butene, 21.6 wt% of cis-2-butene, 36.8 wt% of trans-2-butene and 1.9 wt% of iso-butene.

In the reaction the following proportions and conditions were used: 3.6 g (58.3 mmol) of butenes; 0.656 g (5.8 mmol) of H_2O_2 (as a 30% solution in H_2O); 0.5 g of TS-1 pellets; 50 g methanol; and a CO_2 pressure of 89 bar for 1 hour at 40°C.

The reaction resulted in 98.2% selectivity for the epoxides compared with a selectivity of 93% without the use of carbon dioxide.

Example 5

The general procedure of example 1 was repeated using a cyclopentene feedstock in place of the 1-octene.

In the reaction the following proportions and conditions were used: 3.93 g (58.3 mmol) of cyclopentene, 0.656 g (5.8 mmol) of H_2O_2 (as a 30% solution in H_2O), 0.5 g of TS-1 pellets, 50 g methanol and a CO_2 pressure of 88 bar for 1 hour at 40°C.

The reaction resulted in 94% selectivity for the epoxide compared with a selectivity of 59% without the use of carbon dioxide.

Example 6

The general procedure of example 1 was repeated using a propylene feedstock in place of the 1-octene

In the reaction the following proportions and conditions were used: 2.47 g (58.3 mmol) of propylene, 0.656 g (5.8 mmol) of H_2O_2 (as a 30% solution in H_2O), 0.5 g of TS-1 pellets, 50 g methanol and a CO_2 pressure of 88 bar for 1 hour at 40°C.

The reaction resulted in 100% selectivity for the epoxide compared with a selectivity of 87% without the use of

carbon dioxide.

Example 7

A series of experiments were undertaken using the general procedure of Example 3 at 40°C for 30 minutes, with the exception that for some of the experiments the solvent to 1-octene ratio was decreased. The results are illustrated in Figure 5. These results show that even at low ratios of solvent to substrate the epoxide selectivity and oxidant conversion both remain high.

Claims

1. A process for the conversion of one or more unsaturated hydrocarbons to one or more epoxides which process comprises reacting one or more unsaturated hydrocarbons in a reaction mixture under oxidation conditions in the presence of an oxidant, a heterogeneous catalyst and a solvent characterized in that the catalyst comprises a Group IVB, VB or VIB metal and that carbon dioxide is present in the reaction mixture under supercritical conditions.

2. A process of claim 1 wherein the catalyst is a metal molecular sieve.

3. A. process of claim 2 wherein the metal is a Group IVB metal.

4. A process of claim 3 wherein the metal is titanium.

5. A process of claim 1 wherein the solvent is methanol.

6. A process of claim 1 wherein the oxidant is hydrogen peroxide.

7. A process of claim 1 wherein the unsaturated hydrocarbon is an olefin.

8. A process of claim 1 comprising an additional step wherein the epoxide is converted to one or more acids or alcohols.

9. A process of claim 8 wherein the one or more acids or alcohols are linear acids and linear alcohols.

10. A process of claim 1 wherein the ratio of solvent to unsaturated hydrocarbon is less than 8:1.

EP 0 957 095 A2

11. A process of claim 1 wherein the reaction mixture comprises at least 1% by weight of carbon dioxide.

12. A process of claim 11 wherein the reaction mixture comprises at least 25% by weight of carbon dioxide.

13. A process of claim 1 wherein the carbon dioxide constitutes more than 50% by weight of the solvent used in the reaction mixture.

14. A process of claim 1 wherein the catalyst is selected from one of the following: TS-1, TS-2, TS-3, titanium zeolite beta, TS-48, titanium mordenite and titanium silicalite.

15. A process of claim 1 wherein the reaction residence time is at least 20% less than that required to achieve 50% conversion without the presence of carbon dioxide.

16. A process of claim 15 wherein the reaction residence time is at least 50% less.

17. A process of claim 16 wherein the conversion is at least 90%.

18. A process of claim 1 wherein the reaction pressure is between 1 and 700 atmospheres.

19. A process of claim 1 wherein the epoxidation reaction temperature is from 0°C to 100°C.

20. A process of claim 19 wherein the reaction temperature is within range 40°C to 80°C.

21. A process of claim 1 wherein the reaction residence time is within the range 10 minutes to 48 hours.

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ABSTRACT

Oxidation Process

The selectivity of an olefin epoxidation process catalyzed by a heterogeneous catalyst for example titanium silicalite is improved by performing the epoxidation in the presence of carbon dioxide. The catalysts used do not require regeneration on each recycle.

20060 "5/26/1/50

PATENT COOPERATION TREATY

PCT Rec'd 08 DEC 2000

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
P18056WO		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP99/03998	08/06/1999	08/06/1998
International Patent Classification (IPC) or national classification and IPC C07B33/00		
Applicant EXXON CHEMICAL PATENTS INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 9 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☒ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☒ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
21/12/1999	22.09.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Seelmann, M Telephone No. +49 89 2399 2128

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP99/03998

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1,3-5,7,9-12, 15-21	as originally filed			
2,2a,6,8,13,14	as received on	23/06/2000	with letter of	21/06/2000

Claims, No.:

1-21	as received on	23/06/2000	with letter of	21/06/2000

Drawings, sheets:

1/5-5/5	as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

II. Priority

1. ☐ This report has been established as if no priority had been claimed due to the failure to furnish within the prescribed time limit the requested:

   ☐ copy of the earlier application whose priority has been claimed.

   ☐ translation of the earlier application whose priority has been claimed.

2. ☐ This report has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid.

Thus for the purposes of this report, the international filing date indicated above is considered to be the relevant date.

3. Additional observations, if necessary:

see separate sheet

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1-21
	No:	Claims
Inventive step (IS)	Yes:	Claims 1-21
	No:	Claims
Industrial applicability (IA)	Yes:	Claims 1-21
	No:	Claims

2. Citations and explanations

see separate sheet

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

D1 DE 196 00 709
D2 US 5 210 336
D3 US 4 833 260 cited in the application
D4 DE 197 25 820
D5 DE 197 23 949
D6 US 4 483 996 cited in the application

Item II

Priority

The priority document pertaining to the present application was not available at the time of establishing this report. Hence, it is based on the assumption that all the claims enjoy priority right from the filing date of the priority document. If it later turns out that this is not correct, the documents cited in the international search report as P-document (**D4** and **D5**) could become relevant to assess whether the subject-matter satisfies the criteria set forth in Article 33(1) PCT.

Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

In order to overcome the novelty objection of the Written Opinion, the applicant modified claim 1 by restricting to an epoxidation process (original claim 9) using CO_2 under supercritical conditions (original claim 8). The original claim 14 was deleted to remove the inconsistency with Figure 5. All the indefinite expressions "and/or the like" were removed from the description. D2 was cited on page 2 of the description. These amendements filed with the letter dated on the 21.06.2000 do not introduce new subject-matter which extends beyond the content of the application as originally filed, and therefore fulfill the requirements of Article 34(2)b) PCT.

1. Novelty - Article 33(2) PCT

The epoxidation of olefins in **D1** (claim 1, page 8) is characterized by the use of a Ti catalyst (page 4, lines 38-40) in presence of CO_2 (page 5, lines 67-68 and page 6, lines 1-2) but not in supercritical conditions.

The olefin oxidation at supercritical conditions is known from **D2** using O_2, CO_2, H_2O in the presence of a CuI/Cu_2O catalyst containing no metal of the Group IVB, VB or VIB, to produce the corresponding glycols.
The olefin oxidation of **D3** does use the synthetic zeolites containing titanium silicalites, *i.e.* in particular TS-1, but no CO_2.
The olefin oxidation of **D6** at supercritical conditions uses O_2, CO_2 as solvent and thallous oxide as catalyst (no metal of the Group IVB, VB or VIB).

Novelty could accordingly be recognized for the present process (claims 1-21).

2. Inventive step - Article 33(3) PCT

2.1 The olefin oxidation of **D3** does not use CO_2.

2.2 The technical problem is to find oxidative conditions in order to maintain the catalytic activity in an epoxidation process.

2.3 The solution of the applicant is a process using carbon dioxide under supercritical conditions and a catalyst comprising a group IVB, VB or VIB metal.

2.4 The TS-1 catalyst is used in the epoxidation reaction of **D3** without loss of titanium. It can be totally recovered and reused after each reaction (page 3, lines 30-31). Experiment 3 of the present demand (pg 16-17) corresponds to the conditions of **D3**. Experiment 4 illustrates the process claimed (pg 17-18). Comparing the percentage of conversion of the oxidant upon recycling of the catalyst in both experiments, one notices that the catalyst in experiment 3 suffers a greater loss of activity than in experiment 4, already after the first recycle. This is directly connected with the absence of CO_2 under supercritical conditions.Nothing would have led the man skilled in the art from the teaching of **D3** to the present solution. An inventive step could accordingly be recognized for the the subject-matter of claims 1-21.

Industrial applicability

3. No objection.

Item VI

Certain documents cited

Certain published documents (Rule 70.10)

Application No Patent No	Publication date *(day/month/year)*	Filing date *(day/month/year)*	Priority date *(valid claim)* *(day/month/year)*
D4	24.12.98	18.06.97	
D5	10.12.98	06.06.97	

Item VIII

Certain observations on the international application

In the regional phase, the applicant would have to adapt the description to the new set of claims provided with the letter of 21.06.2000.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03998

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07B33/00 C07D301/12 C07C27/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D C07B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PTO/PCT Rec'd 08 DEC 2000

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 196 00 709 A (BASF AG) 17 July 1997 (1997-07-17) the whole document, particularly column 5, lines 31-49	1-25
Y	US 5 210 336 A (GAFFNEY A M ET AL) 11 May 1993 (1993-05-11) cited in the application the whole document	1-25
Y	US 4 833 260 A (NERI C ET AL) 23 May 1989 (1989-05-23) cited in the application the whole document	1-25
P,X	DE 197 25 820 A (LINDE AG) 24 December 1998 (1998-12-24) the whole document, particularly claim 4	1-25

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 September 1999	15/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Allard, M

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03998

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DE 197 23 949 A (BASF AG) 10 December 1998 (1998-12-10) the whole document, particularly column 12 lines 16-19 in combination with lines 44 and 45	1-25
A	US 4 483 996 A (JACOBSON S E) 20 November 1984 (1984-11-20) cited in the application	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/03998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19600709 A	17-07-1997	NONE	
US 5210336 A	11-05-1993	EP 0385631 A	05-09-1990
		JP 2264734 A	29-10-1990
US 4833260 A	23-05-1989	IT 1152299 B	31-12-1986
		AT 21896 T	15-09-1986
		CA 1196925 A	19-11-1985
		DK 341483 A	29-01-1984
		EP 0100119 A	08-02-1984
		JP 1721832 C	24-12-1992
		JP 4005028 B	30-01-1992
		JP 59051273 A	24-03-1984
DE 19725820 A	24-12-1998	NONE	
DE 19723949 A	10-12-1998	AU 8214098 A	21-12-1998
		WO 9855228 A	10-12-1998
US 4483996 A	20-11-1984	EP 0117147 A	29-08-1984
		JP 59163334 A	14-09-1984

PATENT COOPERATION TREATY

25-02-00 RCVD 0525

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:
White, Nicholas J.
HARRISON GODDARD FOOTE
Windsor House
Cornwall Road
Harrogate HG1 2PN
GRANDE BRETAGNE

PTO/PCT Rec'd 08 DEC 2000

PCT

WRITTEN OPINION

(PCT Rule 66)

Date of mailing *(day/month/year)*	21.02.2000
Applicant's or agent's file reference: P18056WO	**REPLY DUE** **within 3 month(s)** from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP99/03998	08/06/1999	08/06/1998

International Patent Classification (IPC) or both national classification and IPC
C07B33/00

Applicant
EXXON CHEMICAL PATENTS INC.

1. This written opinion is the **first** drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

I	☒	Basis of the opinion
II	☐	Priority
III	☐	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	☐	Lack of unity of invention
V	☒	Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	☐	Certain document cited
VII	☒	Certain defects in the international application
VIII	☒	Certain observations on the international application

3. The applicant is hereby **invited to reply** to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 08/10/2000.

Name and mailing address of the international preliminary examining authority:
European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer / Examiner
Gerzain, M

Formalities officer (incl. extension of time limits)
Pfitzner, G
Telephone No. +49 89 2399 2700

I. Basis of the opinion

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*):

Description, pages:

1-21 as originally filed

Claims, No.:

1-25 as originally filed

Drawings, sheets:

1/5-5/5 as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-12,15-16,18,22-25:no
Inventive step (IS)	Claims	13-14,17,19-21:no
Industrial applicability (IA)	Claims	1-25: yes

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

D1 DE 196 00 709
D2 US 5 210 336
D3 US 4 833 260 cited in the application
D4 DE 197 25 820
D5 DE 197 23 949
D6 US 4 483 996 cited in the application

Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Novelty - Article 33(2) PCT

1. The epoxidation of olefins in **D1** (claim 1, page 8) is characterized by the use of an oxidant (H_2, O_2) in a solvent (MeOH, page 5, lines 41-44) and the presence of a Ti catalyst (page 4, lines 38-40) and CO_2 (page 5, lines 67-68 and page 6, lines 1-2), under a pressure of 1 to 10 bars (page 5, lines 38-41) and a temperature of 20 to 50°C (page 5, lines 50-52). In the same way **D5** describes the epoxidation of unsaturated hydrocarbons (examples 3, 5 and 7) using a regenerated zeolite-catalysator (claims 1, 8 and 10)
   The olefin oxidation at supercritical conditions is known from **D2** using O_2, CO_2, H_2O in the presence of a CuI/Cu_2O catalyst containing no titanium, to produce the corresponding glycols. The olefin oxidation of **D3** does use the synthetic zeolites containing titanium silicalites, *i.e.* in particular TS-1 but no CO_2.
   D4 describes the production of 1,2-diols in two steps; i.e. oxidation of an olefin followed by hydrolysis of the formed epoxide. The oxidation (claims 1 and 9) comprises H_2O_2, a solvent (claims 3-4), a titanium catalyst (claim 5) and CO_2 at the supercritical state.
   The olefin oxidation of **D6** at supercritical conditions uses O_2, CO_2 as solvent and thallous oxide as catalyst.

   All the technical features of the present application are already known from **D1**, **D4** or **D5**. Accordingly novelty could not be recognized for the present process (claims 1-12, 15-16, 18 and 22-25).

Inventive step - Article 33(3) PCT

2. The process in **D2** differs from the one of the present application in the catalyst used.

2.1 The technical problem is to provide another oxidative process.

2.2 The solution of the applicant is a process using carbon dioxide and a catalyst comprising a group IVB, VB or VIB metal with a solvent/substrate ratio less than 8:1.

2.3 To enhance the selectivity in the production of glycols, the presence of CO_2 and supercritical reaction conditions are necessary (**D2**, page 2, lines 18-29 and 34-49). The use of TS-1 catalyst in epoxidation reaction is already known from **D3**, where it can be totally recovered and reused (page 3, lines 30-31). The solvent/substrate ratio is part of the set-up of the experimental conditions known to the skilled person. It would be therefore obvious for the man skilled in the art to combine the teaching of both **D2** and **D3** to come up with the present solution. No inventive step could accordingly be recognized for the the subject-matter of claims 13-14, 17 and 19-21.

Industrial applicability

3. No objection.

Item VII

Certain defects in the international application

1. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the document **D2** is not mentioned in the description, nor is this document identified therein.

Item VIII

Certain observations on the international application

1. The expression "*under oxidation conditions*" is too broad, *i.e.* vague. It is clear from the examples that it relates to the use of a titanium catalyst (i.e. TS-1), H_2O_2 as oxidant and MeOH as solvent in the oxidation of C_2-C_{30} olefins. Since independent

claim 1 does not contain these features, it does not meet the requirement following from Article 6 PCT taken in combination with Rule 6.3(b) PCT that any independent claim must contain all the technical features essential to the definition of the invention.

2. The term "*and/or the like*" used on pages 6, 8 and 13 4 is indefinite and should accordingly be removed from the description. Also, the paragraph on pages 13 (lines 31-34) and 14 (lines 1-2) should be deleted to avoid any ambiguity about the extent of the protection (PCT Guidelines CIII-4.3a).

3. A discrepancy has been noticed between claim 14 and the description/Figure 5. The ratio for solvent ot substrate seems to be between 8:1 and 1:1. There is no evidence in the present demand that a ratio less than 1:1 avoids an inefficient utilisation of the oxidant and side reactions to occur. The applicant is requested to remove this inconsistency, either by amending the claim 14, or the embodiment concerned from the description and the Figure 5 (PCT Guidelines, C-III, 4.3).

3

PATENT COOPERATION TREATY

REC'D 26 SEP 2000

WIPO PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
P18056WO		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP99/03998	08/06/1999	08/06/1998
International Patent Classification (IPC) or national classification and IPC C07B33/00		
Applicant EXXON CHEMICAL PATENTS INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 9 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☒ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☒ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
21/12/1999	22.09.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Seelmann, M Telephone No. +49 89 2399 2128

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP99/03998

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1,3-5,7,9-12, 15-21	as originally filed			
2,2a,6,8,13,14	as received on	23/06/2000	with letter of	21/06/2000

Claims, No.:

1-21	as received on	23/06/2000	with letter of	21/06/2000

Drawings, sheets:

1/5-5/5	as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

II. Priority

1. ☐ This report has been established as if no priority had been claimed due to the failure to furnish within the prescribed time limit the requested:

☐ copy of the earlier application whose priority has been claimed.

☐ translation of the earlier application whose priority has been claimed.

2. ☐ This report has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid.

Thus for the purposes of this report, the international filing date indicated above is considered to be the relevant date.

3. Additional observations, if necessary:

see separate sheet

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-21
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-21
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-21
	No:	Claims	

2. Citations and explanations

see separate sheet

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

D1 DE 196 00 709
D2 US 5 210 336
D3 US 4 833 260 cited in the application
D4 DE 197 25 820
D5 DE 197 23 949
D6 US 4 483 996 cited in the application

Item II
Priority

The priority document pertaining to the present application was not available at the time of establishing this report. Hence, it is based on the assumption that all the claims enjoy priority right from the filing date of the priority document. If it later turns out that this is not correct, the documents cited in the international search report as P-document (**D4** and **D5**) could become relevant to assess whether the subject-matter satisfies the criteria set forth in Article 33(1) PCT.

Item V
Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

In order to overcome the novelty objection of the Written Opinion, the applicant modified claim 1 by restricting to an epoxidation process (original claim 9) using CO_2 under supercritical conditions (original claim 8). The original claim 14 was deleted to remove the inconsistency with Figure 5. All the indefinite expressions "and/or the like" were removed from the description. D2 was cited on page 2 of the description. These amendements filed with the letter dated on the 21.06.2000 do not introduce new subject-matter which extends beyond the content of the application as originally filed, and therefore fulfill the requirements of Article 34(2)b) PCT.

1. Novelty - Article 33(2) PCT

The epoxidation of olefins in **D1** (claim 1, page 8) is characterized by the use of a Ti catalyst (page 4, lines 38-40) in presence of CO_2 (page 5, lines 67-68 and page 6, lines 1-2) but not in supercritical conditions.

The olefin oxidation at supercritical conditions is known from **D2** using O_2, CO_2, H_2O in the presence of a CuI/Cu_2O catalyst containing no metal of the Group IVB, VB or VIB, to produce the corresponding glycols.
The olefin oxidation of **D3** does use the synthetic zeolites containing titanium silicalites, *i.e.* in particular TS-1, but no CO_2.
The olefin oxidation of **D6** at supercritical conditions uses O_2, CO_2 as solvent and thallous oxide as catalyst (no metal of the Group IVB, VB or VIB).

Novelty could accordingly be recognized for the present process (claims 1-21).

2. Inventive step - Article 33(3) PCT

2.1 The olefin oxidation of **D3** does not use CO_2.

2.2 The technical problem is to find oxidative conditions in order to maintain the catalytic activity in an epoxidation process.

2.3 The solution of the applicant is a process using carbon dioxide under supercritical conditions and a catalyst comprising a group IVB, VB or VIB metal.

2.4 The TS-1 catalyst is used in the epoxidation reaction of **D3** without loss of titanium. It can be totally recovered and reused after each reaction (page 3, lines 30-31). Experiment 3 of the present demand (pg 16-17) corresponds to the conditions of **D3**. Experiment 4 illustrates the process claimed (pg 17-18). Comparing the percentage of conversion of the oxidant upon recycling of the catalyst in both experiments, one notices that the catalyst in experiment 3 suffers a greater loss of activity than in experiment 4, already after the first recycle. This is directly connected with the absence of CO_2 under supercritical conditions.Nothing would have led the man skilled in the art from the teaching of **D3** to the present solution. An inventive step could accordingly be recognized for the the subject-matter of claims 1-21.

Industrial applicability

3. No objection.

Item VI

Certain documents cited

Certain published documents (Rule 70.10)

	Application No Patent No	Publication date *(day/month/year)*	Filing date *(day/month/year)*	Priority date *(valid claim)* *(day/month/year)*
D4		24.12.98	18.06.97	
D5		10.12.98	06.06.97	

Item VIII

Certain observations on the international application

In the regional phase, the applicant would have to adapt the description to the new set of claims provided with the letter of 21.06.2000.

utilises a chelating agent to reduce the catalysts tendency to non-selectively decompose the hydrogen peroxide oxidant used. EP 0 385 631 A1 describes an oxidation process for the conversion of olefins to glycols utilising oxygen and carbon dioxide as reactants under supercritical conditions. A heterogeneous copper containing catalyst is proposed. U.S. Pat. No. 5,646,314 proposes performing the oxidation reaction in the presence of nonbasic salts in order to improve selectivity.

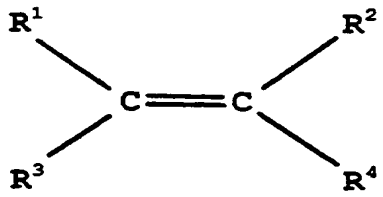
Furthermore it has long been recognised that metal containing zeolite catalysts rapidly become deactivated in use. There have been a number of methods developed to counter this deactivation and/or to regenerate the catalyst after use. U.S. Pat. No. 5, 741, 749 proposes a the regeneration of a titanium containing molecular sieve oxidation catalyst by treatment with a gas stream comprising specific amounts of molecular oxygen. WO 98/18555 proposes the regeneration of a titanium silicalite catalyst with a liquid solution of an oxidising agent. WO 98/ 18556 proposes the regeneration of a titanium silicalite catalyst under a specific gas flow

In US 5 210 336 a process is described for the conversion of olefins to glycols utilising a CuI/Cu_2O catalyst. The reaction is undertaken in the presence of carbon dioxide which acts as a solvent and a co-reactant, under supercritical conditions.

There are a number of problems with the processes of the prior art. Conversions and selectivities for the various reactions are in general still low or require additional process modifications which incur additional

costs. Frequently the catalyst systems utilised require special treatments and/or frequent regeneration in order to maintain catalyst activity.

It has been surprisingly found that the conversion and selectivity of oxidation processes, in particular the



wherein R^1, R^2, R^3, and R^4 are the same or different and are selected from the group consisting of hydrogen and C_1-C_8 alkyl (selected so that the total number of carbons in the olefin does not exceed 30).

The process of this invention is also suitable for use in epoxidizing olefins containing functional groups other than aliphatic hydrocarbyl moieties. For example, the carbon-carbon double bond can be substituted with groups such as $-CO_2H$, $-CO_2R_1$, -CN, or -OR wherein R is an alkyl, cycloalkyl, aryl or aralkyl substituent. The radicals R^1, R^2, R^3, and R^4 in the structural formula shown hereinabove may contain aryl, aralkyl, halo, nitro, sulfonic, cyano, carbonyl, (e.g. ketone, aldehyde,) hydroxyl, carboxyl (e.g ester, acid) or ether groups. Examples of olefins of these types include allyl alcohol, styrene, allyl chloride, allyl methyl ether, allyl phenyl ether, methyl methacrylate, acrylic acid, methyl acrylate, and stilbene.

The amount of hydrogen peroxide relative to the

minor amounts of boron, iron, and aluminum may be present.

Titanium silicalite catalysts suitable for use in the process of this invention will generally have a composition corresponding to the following empirical formula $xTiO_2:(1-x)SiO_2$, where x is between 0.0001 and 0.500. More preferably, the value of x is from 0.01 to 0.125. The molar ratio of Si:Ti in the lattice framework of the titanium silicalite is advantageously from 9.5:1 to 99:1 (most preferably, from 9.5:1 to 60:1). The use of relatively titanium-rich silicalites may also be desirable. The preferred catalyst is titanium silicalite-1. One form of catalyst suitable for use in the process of the present invention is a "cherry type" catalyst which consists of a core of material e.g. silica/alumina and a shell of different material e.g. silica/titania as described for example in EP 634 212. The titanium silicalite catalyst may be incorporated in or in the form of a membrane; for example TS-1 or Ti-MCM-41 may be occluded in polydimethylsiloxane (PDMS) membranes, as described in Chemical Communications (1997) pages 137 to 138.

The amount of catalyst employed is not critical, but should be sufficient so as to substantially accomplish the desired epoxidation reaction in a particularly short period of time. The optimum quantity of catalyst will depend upon a number of factors including reaction temperature, olefin reactivity and concentration, hydrogen peroxide concentration, type and concentration of organic solvent as well as catalyst activity and the type of reactor or reaction system (i.e. batch vs continuous) employed. In a batch-type or slurry reaction, for example, the amount of catalyst will

desired degree of conversion, the epoxide product may be separated and recovered from the reaction mixture using any appropriate technique such as fractional distillation, extractive distillation, liquid-liquid extraction, or crystallisation. After separating from the epoxidation reaction mixture by any suitable method such as filtration (as when a slurry reactor is utilised, for example), the recovered titanium silicalite catalyst may be economically re-used in subsequent epoxidations. Where the catalyst is deployed in the form of a fixed bed, the epoxidation product withdrawn as a stream from the epoxidation zone will be essentially catalyst free with the catalyst being retained within the epoxidation zone. Similarly, any unreacted olefin or hydrogen peroxide may be separated and recycled or otherwise disposed of. In certain embodiments of the instant process where the epoxide is produced on a continuous basis, it may be desirable to periodically or constantly regenerate all or a portion of the used catalyst in order to maintain optimum activity and selectivity. Suitable regeneration techniques are well-known and include, for example, calcination and solvent treatment. Such regeneration and/or treatment may not be necessary until a significant number of recycles have occurred through the process of the present invention. Typical examples of suitable regeneration methods are provided in WO99/01445, WO98/18556, WO98/28072 and Journal of Molecular Catalysis A:Chemical 117 (1997) 351-356. The disclosures of each of these references are incorporated by reference.

The present invention is further illustrated by means of the following examples:

Example 1

A TS-1 catalyst (prepared by the procedure given in Applied Catalysis, 99, (1993), pages 71-84) was utilised in the oxidation of 1-octene to 1,2-epoxyoctane with and without supercritical carbon dioxide as the solvent. A 250 cm^3 batch autoclave equipped with a temperature controller, mechanical stirrer (1000 rpm), reagents feed line, sampling line and vent line was charged in two separate experiments with the following reagents.

Reagents	Experiment 1	Experiment 2
	Weight (g)	Weight (g)
1-octene	14.52	7.26
H_2O_2 (30wt% in H_2O)	0.44*	0.22*
Methanol	112.5	56.25
Carbon Dioxide	0	74.2
TS-1 catalyst	1.0	0.5
Total	128.46	138.43

*= the weight of H_2O_2 does not include the weight of H_2O

For Experiment 1 the reaction was undertaken at 65°C for 60 minutes. For Experiment 2 the reactor was first pressurised with carbon dioxide gas to 48 bar (48 x 10^5 Nm^{-2}), after which 74.2g of liquid carbon dioxide was

Claims

7. 1. A process for the conversion of one or more unsaturated hydrocarbons to one or more epoxides which process comprises reacting one or more unsaturated hydrocarbons in a reaction mixture under oxidation conditions in the presence of an oxidant, a heterogeneous catalyst and a solvent characterised in that the catalyst comprises a Group IVB, VB or VIB metal and that carbon dioxide is present in the reaction mixture under supercritical conditions.

2. A process as claimed in claim 1 wherein the catalyst is a metal molecular sieve.

3. A process as claimed in claim 1 or claim 2 wherein the metal is a Group IVB metal.

4. A process as claimed in claim 3 wherein the metal is titanium.

5 A process as claimed in any one of claims 1 to 4 wherein the solvent is methanol.

6. A process as claimed in any of the preceding claims wherein the oxidant is hydrogen peroxide.

7. A process as claimed in any one of the preceding claims wherein the unsaturated hydrocarbon is an olefin.

8. A process as claimed in any one of claims 1 to 7 comprising an additional step wherein the epoxide is converted to one or more acids or alcohols.

9. A process as claimed in claim 8 wherein the one or more acids or alcohols are linear acids and linear alcohols.

10. A process as claimed in any of the preceding claims wherein the ratio of solvent to unsaturated hydrocarbon is less than 8:1.

11. A process as claimed in any of the preceding claims wherein the reaction mixture comprises at least 1% by weight of carbon dioxide.

12. A process as claimed in claim 11 wherein the reaction mixture comprises at least 25% by weight of carbon dioxide.

13. A process as claimed in any of the preceding claims wherein the carbon dioxide constitutes more than 50% by weight of the solvent used in the reaction mixture.

14. A process according to any one of claims 4 to 13 wherein the catalyst is selected from one of the following: TS-1, TS-2, TS-3, titanium zeolite beta, TS-48, titanium mordenite and titanium silicalite.

15. A process according to any of claims 1 to 14 wherein the reaction residence time is at least 20% less than that required to achieve 50% conversion without the presence of carbon dioxide.

16. A process according to claim 15 wherein the reaction residence time is at least 50% less.

17. A process according to either claim 15 or claim 16 wherein the conversion is 90%.

18. A process as claimed in any of the preceding claims wherein the reaction pressure is between 1 and 700 atmospheres.

19. A process as claimed in any of the preceding claims wherein the epoxidation reaction temperature is from 0°C to 100°C.

20. A process as claimed in claim 19 wherein the reaction temperature is within the range 40°C to 80°C.

21. A process as claimed in any of the preceding claims wherein the reaction residence time is within the range 10 minutes to 48 hours.

PCT/EP99/03998

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 08 February 2000 (08.02.00)	
International application No. PCT/EP99/03998	**Applicant's or agent's file reference** P18056WO
International filing date (day/month/year) 08 June 1999 (08.06.99)	**Priority date** (day/month/year) 08 June 1998 (08.06.98)
Applicant DAKKA, Jihad et al	

1. The designated Office is hereby notified of its election made:

   [X] in the demand filed with the International Preliminary Examining Authority on:

   21 December 1999 (21.12.99)

   [ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

   [ ] was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Claudio Borton
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
P18056WO		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP 99/ 03998	08/06/1999	08/06/1998
Applicant		
EXXON CHEMICAL PATENTS INC.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [ ] the text is approved as submitted by the applicant.

   [X] the text has been established by this Authority to read as follows:

   OXIDATION PROCESS IN THE PRESENCE OF CARBON DIOXIDE

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. _____

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03998

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07B33/00 C07D301/12 C07C27/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D C07B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 196 00 709 A (BASF AG) 17 July 1997 (1997-07-17) the whole document, particularly column 5, lines 31-49	1-25
Y	US 5 210 336 A (GAFFNEY A M ET AL) 11 May 1993 (1993-05-11) cited in the application the whole document	1-25
Y	US 4 833 260 A (NERI C ET AL) 23 May 1989 (1989-05-23) cited in the application the whole document	1-25
P,X	DE 197 25 820 A (LINDE AG) 24 December 1998 (1998-12-24) the whole document, particularly claim 4	1-25

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 September 1999	15/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Allard, M

1

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	DE 197 23 949 A (BASF AG) 10 December 1998 (1998-12-10) the whole document, particularly column 12 lines 16-19 in combination with lines 44 and 45	1-25
A	US 4 483 996 A (JACOBSON S E) 20 November 1984 (1984-11-20) cited in the application	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/03998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19600709 A	17-07-1997	NONE	
US 5210336 A	11-05-1993	EP 0385631 A	05-09-1990
		JP 2264734 A	29-10-1990
US 4833260 A	23-05-1989	IT 1152299 B	31-12-1986
		AT 21896 T	15-09-1986
		CA 1196925 A	19-11-1985
		DK 341483 A	29-01-1984
		EP 0100119 A	08-02-1984
		JP 1721832 C	24-12-1992
		JP 4005028 B	30-01-1992
		JP 59051273 A	24-03-1984
DE 19725820 A	24-12-1998	NONE	
DE 19723949 A	10-12-1998	AU 8214098 A	21-12-1998
		WO 9855228 A	10-12-1998
US 4483996 A	20-11-1984	EP 0117147 A	29-08-1984
		JP 59163334 A	14-09-1984